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

**EXECUTIVE SUMMARY**

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**CLAM FINAL SUMMARY REPORT**

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## **Scope of the Executive Summary Report**

This report summarises the work carried out under the DETR research contract “Acidification of Freshwaters: the Role of Nitrogen and Prospects for Recovery” (EPG 1/3/117), also referred to as the CLAM (Critical Loads of Acidity and Metals) Project. Since the work programme was very wide-ranging and the data and written outputs very large, it is summarised in this report at three levels. First, the Executive Summary provides a very concise, two-page summary of the major research findings under each of three Work Packages; Nitrogen, Recovery and Metals. This is followed by the detailed Technical Summary, which first lists the Key Points to emerge from each Work Package, and then provides a more detailed summary of the work completed and the conclusions to be drawn.

The data and graphical outputs for every Task under each of the Work Packages are reported separately in three extensive documents which accompany this Executive Summary.

## EXECUTIVE SUMMARY

### 1. Modelling N retention and leaching

This work package addressed some of the problems associated with modelling potential impacts of N deposition on the acidification status of upland waters. Intensive field measurements and laboratory based experimental studies, in combination with extensive regional survey data, have provided further insights into the processes regulating the storage and leaching of N within upland catchments.

Denitrification was found to cause only a minor loss of deposited N, and the model recommended by the UNECE Mapping Manual for critical loads produces denitrification rates far higher than those observed. It is therefore recommended that the low, soil-specific, literature derived values for denitrification produced under the Terrestrial Umbrella programme for critical loads should continue to be used in freshwater critical loads modelling in the UK.

Low denitrification rates in upland catchments provide further evidence that the high observed rates of N retention must be due to immobilisation processes in soils. Extensive regional survey work and intensive sampling within the Lochnagar catchment showed a high degree of spatial variability in soil C and N content both within and between different soil types. In peaty soils much of the organic matter is chemically inert, which may explain why the whole soil C/N ratio is found to be a poor predictor of N leaching from moorland soils. However, intensive studies down soil profiles at four experimental catchments showed that the C/N ratio of the top 5cm of soil profiles, which generally comprises the active soil organic horizon, may be much more closely linked to soil N processes such as mineralization, nitrification and immobilization and may have some potential as an indicator of N leaching, particularly from non-peat soils.

MAGIC modelling work has shown that changes in whole soil C/N ratio, which were thought to be a prerequisite for the high rates of nitrate leaching predicted by the steady-state FAB model, would take perhaps centuries to attain, but future dynamic modelling work will have to focus on adequate representation of the key factors controlling N processes in the *active* soil C and N pools, which are likely to be much smaller than the inactive pools. Problems of catchment heterogeneity might be addressed through a novel method of calibrating MAGIC to 'landscape types' rather than whole catchments. If landscape units can be shown to have more homogenous C and N characteristics, this approach could have great potential for more accurate simulation of the dynamics of N leaching. However, the importance of current commitments to reduce S deposition under the Gothenburg Protocol were demonstrated by MAGIC7 modelling which showed that planned S reductions have a greater impact on predicted ANC than even the worst case N leaching scenario over the next 50 years.

### 2 Measuring and modelling recovery

Reviews of existing studies showed that biological recovery from the large-scale, long-term impacts of freshwater acidification could require proportionately long time scales, perhaps centuries. Attempts to measure and model recovery over more practical timescales should therefore consider damage reversal towards some target endpoint rather than true repair or restoration. In aquatic systems several factors could

cause a time lag in recovery, and experiments at Llyn Brianne demonstrated that hysteresis in recovery after liming reflects limited persistence of organisms rather than restricted dispersal. The continued effects of acid episodes in systems undergoing chemical recovery could be a major factor in this hysteresis. This is demonstrated by the significant improvement of regression models which predict biological status from modal chemistry in Welsh Acid Waters Survey (WAWS) stream sites when indices of pH and aluminium episodicity are included.

Data from the WAWS and the Acid Waters Monitoring Network demonstrated that between-year variation in biological communities (invertebrates and diatoms) may be linked to climatic fluctuations driven by the North Atlantic Oscillation (NAO) and this could confound attempts to detect biological recovery. Evidence for slight recovery in primary producers has been found in high resolution, integrated sediment trap and sediment core diatom data from some of the Galloway cluster sites, but the data further support the conclusion that biological recovery is likely to be slow.

Recovery targets and management strategies for acidified freshwaters are likely to be driven increasingly by the Water Framework Directive, and require knowledge of reference conditions prior to acidification. Since there are very few data on the pre-acidification status of surface waters for either chemistry or biology, other means have been developed for identifying recovery targets. This programme built on the analogue matching technique for diatoms, whereby their fossil remains in the sediments of acidified lakes are matched to modern assemblages in other (analogue) lakes, to link the current chemistry of the analogue site to the historic, pre-acidification chemistry of the damaged site. The technique has been expanded to include cladoceran remains as well as diatoms, and to identify biological as well as chemical analogues. With this method, the biology of analogue sites can be used to identify potential biological targets for recovery in acidified lakes. The method is restricted to lakes because of the need for a fossil sediment record. It was found to be robust and reliable for a number of lakes from the Acid Waters Monitoring Network, with analogues identified in the less impacted areas of north-west Scotland.

In a complementary approach, logistic regression models to predict biological status from modelled chemical status were further developed for different organisms. In this way, MAGIC has been used to make biological predictions for several regions of the UK under the Gothenburg Protocol, and predictions indicate only partial recovery at just half of sites in some regions. Furthermore, the approach has not yet been developed to account for the problems of biological hysteresis following chemical recovery mentioned above.

### **3 Metal deposition and cycling at Lochnagar**

A scoping study produced under this programme summarised evidence that emissions of metals are generally decreasing but that meteorological conditions exert a major influence and must be taken into account in trend analysis. At Lochnagar, mercury deposition appears to have increased over the last 3 years. There is also evidence that some metals are largely retained in catchment soils there, so that climatic changes could affect lakewater levels of metals, for example through changes in soil erosion. Mosses were found to best reflect trends in deposition of metals, while sediment trap techniques were shown to have great potential for monitoring lakewater metal trends while accounting for catchment inputs.

## TECHNICAL SUMMARY

The technical summary draws out the key points from each work package. These key points are listed below for each work package, followed by the technical summary.

### **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  $ANC_{crit} = 20 \mu\text{eq l}^{-1}$ .
- 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.

### **Recovery: key points**

#### *Hysteresis and problems in detecting biological recovery*

- 1) In the UK, the effects of acidification have been unique in combining impacts on ecosystems that are both large-scale and long-term: existing studies suggest that effects of this type require proportionately long time scales for recovery (i.e. decades-centuries).
- 2) Since ecosystem structures and/or functions might not return to pre-disturbance conditions within practically measurable timescales, “recovery” should, at best, be considered as damage reversal towards some target endpoint rather than true repair or restoration.
- 3) Understanding of functional indicators of recovery (e.g. production, decomposition, predator-prey interactions) is particularly weak.



- 4) In aquatic systems, several factors could cause a time lag in recovery, including the persistence of acid episodes, organism dispersal, the need for recovery across the whole food web to restore functional integrity, and intrinsic limits on population rates of recovery.
- 5) Liming experiments at Llyn Brianne have demonstrated that hysteresis in recovery after liming reflects limited persistence rather than restricted dispersal, and could be due to the continued effects of acid episodes.
- 6) In a study of 70 Welsh streams, indices of pH and Al episodicity significantly improved regression models that predicted biological status over models based on modal chemistry values alone.
- 7) Evaluation of data from upland Welsh streams (Welsh Acid Waters Survey) found that large variations between years in the persistence of invertebrate communities are not entirely stochastic, instead varying with environmental fluctuations, in particular the NAO, which might confound or obscure recovery from acidification.

#### *Defining targets and management for recovery*

- 1) Should forecasts and rates of change due to deposition reduction be limited or slow, interventionist management may be considered by some agencies, e.g. liming, species re-introductions, or agri-environment schemes.
- 2) The Water Framework Directive is likely to drive targets and prescriptions that require us to establish reference conditions for surface waters prior to acidification. It will also require management strategies that promote recovery. A range of uncertainties currently affect our abilities in this regard.
- 3) 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, based on the technique of analogue matching of lake sediment diatom assemblages.
- 4) Analogue matching 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.
- 5) A new approach was applied to 8 AWMN lakes using both diatoms and cladocera, and close modern analogues were identified for 7 out of 8 AWMN lakes studied, with the majority of the analogues located in North and Northwest Scotland, areas of low sulphur and nitrogen deposition.
- 6) Comparison of the chemistry and catchment characteristics of the AWMN lakes to those of the modern analogues showed that the modern analogues had higher lake water pH and alkalinity levels and lower aluminium concentrations, but very similar ionic strength and calcium concentrations.

- 7) These results indicate that the analogue matching approach using diatom and cladoceran remains is a simple, robust and reliable method of identifying modern analogues for acidified lakes in upland areas of the UK, which provide suitable reference conditions for pristine upland lake ecosystems and may be used to evaluate progress made towards restoration in acidified lakes.

#### *Chemical and biological trends*

- 1) An assessment of long-term Galloway data shows that the time-scale and start /end point of the time series has a major bearing on conclusions regarding recovery. Step-changes in the deposition pattern and climatic variations have directly influenced the recovery signal in these sensitive lochs and streams. Nevertheless, these waters are currently at their healthiest point of recovery since 1978.
- 2) Recent trends in sedimentary diatom assemblages in five acidified lochs in Galloway indicate that two sites are recovering strongly while one shows no evidence of recovery. At the remaining two sites, slight species changes could not be confidently ascribed to a recovery response. Here, the influence of inter-annual variation in climatic factors on acidity during the growth season may currently outweigh any benefit of a reduction in anthropogenic acidity.

#### *Chemical and biological modelling of recovery*

- 1) The CLAG/CLAM chemical-biological database was expanded and used to develop predictive models for three biological targets, the diatom *Achnanthes minutissima*, the invertebrate *Baetis rhodani* and an acid tolerant diatom assemblage, using pH and ANC.
- 2) The fitted logistic regression models can predict the occurrence of the target organisms with an internal success rate of c. 70%, and provide a means of predicting the probability of occurrence of the target organisms from modelled hindcasts and forecasts.
- 3) Application of the models to the CLAM national chemical database using an SSWC model hindcast of baseline (pre-industrial), measured present, and FAB modelled future (Gothenburg scenario) ANC indicates substantial biological change in the areas of known acidification (SW England, Wales, Cumbria, Pennines and large parts of Scotland, but virtually complete biological recovery (with no timescale given) under the Gothenburg scenario.
- 4) Biological predictions for five MAGIC5 regions (Cairngorms, Galloway, Pennines, Wales, Lake District) show similar patterns of biological change between baseline and present, with varying degrees of loss of sensitive taxa. Predictions for recovery under the Gothenburg scenario indicate that only partial recovery will take place by 2050, and for some regions sensitive taxa are predicted

only to return to approximately half of the sites inhabited prior to the onset of acidification.

- 5) The biological models provide a simple but robust way to convert hydrochemical hindcasts and forecasts into measures of biological change, and in particular, to assess biological damage under different emission reduction scenarios. There is now a need to validate the models using independent field data, and to increase data coverage in some areas to extend the models to other biological groups e.g. macrophytes.
- 6) Site-specific MAGIC7 applications to the AWMN sites clearly demonstrate the benefit of the emission reductions in both S and N under the Gothenburg Protocol over making no further emission reductions, but the 'best' and 'worst' cases for N leaching have a less significant impact on predicted ANC up to 2041 than the agreed S reductions.
- 7) Regional simulations with MAGIC7 in Galloway, Wales and the south Pennines show marked variability between regions, with potential increases in N leaching having significant implications for recovery only in the Pennines.
- 8) MAGIC7 simulations carried out under different forestry scenarios for the Galloway dataset indicate that immediate replanting of forest after harvesting (worst case) severely curtails recovery in surface water ANC under the REF scenario, while reversion to moorland after harvesting (best case) leads to significant recovery in ANC.

### **Metals: key points**

#### *Scoping study*

- 1) A scoping study was completed to provide an overview of current knowledge on UK temporal and spatial trends in trace metals, monitoring and the potential for setting critical loads.
- 2) Decreasing trends in emissions have been identified most clearly in the UK's longest running metal monitoring programme, the Rural Network, with decreasing concentrations in chromium, nickel, copper, arsenic, vanadium, zinc and lead deposition.
- 3) Atmospheric transport and deposition in the UK are heavily influenced by meteorological conditions and assessment of depositional trends must take these into account. Similarly, future climate change could potentially have a major impact on inputs to freshwaters, particularly with respect to the release of catchment stored metals.
- 4) Several methods are available for assessment of metal deposition trends, including terrestrial mosses, sediment trap samples, dated lake sediments and analysis of standing waters.

- 5) In the definition of metals critical loads there is still much to be done, including the provision of a unified critical loads methodology; the selection of suitable receptor organisms and setting of critical limits; and the collection of suitable model input data.

*Metal deposition and cycling at Lochnagar*

- 1) Mercury data from Lochnagar suggest that atmospheric deposition has increased over the last three years. However, a longer dataset is needed to follow, and confirm, this trend.
- 2) Mercury deposition concentrations are greater than their equivalent lake water concentrations and this suggests that Hg is bound and stored in catchment soils, which implies that it could be released via soil erosion as a result of, for example, future climate change.
- 3) Other trace metals show a decline in deposition at Lochnagar, and all except Pb show a decline in lake water concentrations.
- 4) Most terrestrial plant species followed similar decreasing trends to those of atmospheric deposition, particularly *Hylocomium splendens* and *Pleurozium schreberi*.
- 5) Other terrestrial and aquatic plants showed less agreement with depositional trends, while epilithic diatoms on artificial substrates showed limited usefulness primarily due to the low amounts of material produced.
- 6) Sediment traps show very good potential for monitoring lake metal trends and suggest catchment inputs may be very important.

## **SUMMARY BY WORK PACKAGE**

**This section summarises the work conducted and the main findings under each work package. Separate reports are available covering each work package in more detail and presenting all the data.**

## 1 NITROGEN

### Rationale

The significant role of nitrogen deposition in the acidification of surface waters had already been demonstrated in earlier DETR funded work programmes, which found that nitrate was an important acid anion in many upland waters where atmospheric deposition was the only major source. While strategies for the reduction of sulphur emissions had already been developed and implemented internationally to guarantee a decline in surface water sulphate concentrations, the *future* role of nitrogen deposition in acidification, or more specifically, prospects for recovery from acidification, was less certain.

It was immediately obvious from existing national datasets that if nitrate concentrations remained constant over the next 10-20 years, it would become the major acid anion in many acidified lakes and streams as sulphate levels declined in line with stringent emissions reductions. In addition, the concept of nitrogen saturation was being discussed, along with its implications for possible future increases in nitrate leaching even at constant deposition levels.

While a critical load model for combined sulphur and nitrogen deposition, the First-order Acidity Balance (FAB) model, has been available for several years, it employs a simple mass-balance for nitrogen with very large uncertainties attached to several of the sink terms. The basis of the model is that processes which retain or remove N also retain the associated acidity (protons). The model itself did little to increase confidence in possible future scenarios of nitrate leaching, but it did provide an estimate of the potential magnitude of the problem, in effect a “worst-case scenario”. The key question was then whether the FAB scenario over-protected for nitrogen deposition, or whether the current rates of nitrogen retention and removal were unsustainable so that nitrogen saturation would lead to major increases in nitrate leaching and further acidification.

The same uncertainties applied also to dynamic models, where there was the additional issue of needing to describe rates of change.

The main focus of this part of the work programme was therefore the study of the key nitrogen sink processes to improve their parameterisation in static and dynamic models. The work programme was structured around the following tasks:

1. Review of literature on key nitrogen processes and feasibility study into the use of alternative models.
2. Intensive study of N processes at a small number of key sites.
3. Extensive studies of surface water nitrate and soil C:N ratios in key regions.
4. Testing of results against existing FAB model formulation.
5. Improvement of parameterisation of N processes in MAGIC.

The results of these tasks are summarised below.

## 1.1 Review values for catchment N sinks reported in 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 work already undertaken on forestry as part of the Terrestrial Umbrella programme – “Terrestrial Effects of Acid Pollutants – phase V”, DETR contract EPG 1/3/124, and its related projects funded by the EU and the power industry, e.g. NITREX), 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>). These rates are consistent with those derived from earlier reviews carried out elsewhere, including the Critical Loads Status Report produced for DETR by the National Focal Centre at CEH Monks Wood, which provided the default values employed in previous UK FAB model applications.

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

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 (runoff per unit area). 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 FAB 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 ( $S_S = 0.5$ ,  $S_N = 2\text{-}8 \text{ m yr}^{-1}$ ) should therefore continue to be used for UK lakes while site specific values are being derived.

### *1.1.3 N immobilisation*

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

## **1.2 Feasibility study for the use of HOST for characterisation 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 have been calculated using an integrated approach comprising i) HOST (Hydrology of Soil Types) classification, ii) a Soil Wetness classification, and iii) estimates of denitrification derived from literature.

The strong association between the HOST class and Soil Wetness Class for each soil 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.

Denitrification rates derived from an extensive literature search of 'natural' soils have been assigned to each of the six Soil Wetness Classes. Denitrification rates at catchment scale can therefore be 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.

This technique provides a complementary method to the use of figures assigned for each soil type derived in a previous literature review study (Terrestrial Umbrella) for the calculation of catchment specific denitrification rates which can be used in static critical loads and dynamic modelling.

### **1.3 Evaluation of N dynamics at a catchment scale for at least 4 catchments across a gradient of N leaching relative to deposition**

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 (1995-97 mean N deposition = 7.3 kgN ha<sup>-1</sup> yr<sup>-1</sup>)*

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 NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. Likewise, soilwater concentrations of inorganic N are very low, with a mean value of zero for NO<sub>3</sub><sup>-</sup>. The general lack of available inorganic N is confirmed by KCl extractions of the soils, with very low values for both NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> compared with other sites. Only in the valley peat soils (M2) are appreciable levels of extractable NH<sub>4</sub><sup>+</sup> 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, indicating that here the process is limited by nitrogen availability.

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 NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> followed by immobilisation in soil organic matter.

*Afon Gwy(1995-97 mean N deposition = 27 kgN ha<sup>-1</sup> yr<sup>-1</sup>)*

When the Gwy was selected as a CLAM N budget site, it was thought to experience a fairly high total N deposition load, which, nevertheless, was much lower 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 kgN ha<sup>-1</sup> yr<sup>-1</sup>, 80% of the load at the Etherow. The catchment leaks NO<sub>3</sub><sup>-</sup> during the winter but very little during the

summer, leading to a mean annual value of only 6  $\mu\text{eq l}^{-1}$ . Concentrations of  $\text{NH}_4^+$  are generally below the detection limit of 0.01  $\text{mg N l}^{-1}$ .

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 (1995-97 mean N deposition = 33.6  $\text{kg N ha}^{-1} \text{ yr}^{-1}$ )*

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* (1995-97 mean N deposition =  $33.8 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ )

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 different 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 soil-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. It could 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 (National Power Contract Number MP/82914 – manuscripts in preparation for June 2002).

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.

## 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 1997 and 1998 organic soil samples were collected from moorland and forested areas within the 59 catchments in Galloway for which previous water chemistry data were available. Organic soil C and N content of the samples was analysed and the data used to calculate catchment C/N ratios through a spatial weighting procedure. Water samples were analysed for a full set of chemical determinands.

Surface water data for the South Pennines 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 ( $\text{xSO}_4$ ) concentrations and a high proportion of N inputs transferred to runoff.  $\text{NH}_4^+$  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).

### 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 ( $\text{N}_{\text{OUT}}/\text{N}_{\text{IN}}$ ) 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  $\text{N}_{\text{OUT}}/\text{N}_{\text{IN}}$  based on measured surface water nitrate ( $\text{NO}_3^-$ ), runoff estimates based on CEH 1km interpolated rainfall and evapotranspiration, and UK gridded  $\text{NO}_x$  and  $\text{NH}_x$  deposition. In practice, variations in  $\text{N}_{\text{OUT}}/\text{N}_{\text{IN}}$  within a region were a function primarily of  $\text{NO}_3^-$  concentrations. Results suggest that, on a regional scale, it is difficult to detect the expected relationship between C/N and  $\text{N}_{\text{OUT}}/\text{N}_{\text{IN}}$ . It appears that, although the highest rates of N leaching in all 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, including samples collected at the Welsh UKAWMN sites and in the Lake District, shows 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.

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.

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.

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 include:

- chemical separation of active (labile) and inactive (refractory) organic matter prior to C and N analysis;
- use of 'proxy' measures of soil nitrogen status e.g. N content of vegetation; or
- use of runoff DOC/DON to reflect the 'active' C/N ratio of the catchment.

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.

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

This study was carried out in the Lochnagar catchment (NO 252 859), located in NE Scotland on the Eastern edge of the Cairngorm Mountains. 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.

The sampling 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. 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, and analysed for C and N.

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.

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. The greatest deviation in the C/N ratio is apparent for samples collected from organic soils (i.e. shallow and deep peat). In the absence of field measurements, the bulk density of the organic compartment was estimated ( $150 \text{ kgm}^{-3}$ ), whilst the depth the organic horizons was measured in the field. These data were spatially weighted according to the area of different soil types to calculate the carbon and nitrogen .

In the second method, the geometric mean of point C and N data were calculated based on the number of samples occurring within each class of the topographic model.



C and N pools are calculated using the same soil depth and bulk density information as described in the approach above.

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

While both methodologies gave rise to similar 'surface' organic pools, the calculation of 'total' organic pools was greatest when the topographic model was utilised. The large 'total' C pool derived from the topographic methodology ( $967 \text{ mol/m}^2$ ) is 'representative' of a catchment dominated by thin soils, and extensive areas of exposed rock, when compared with similar European studies. 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.

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 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.

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

### *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 (the successor to MAGIC-WAND) 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. The inclusion of dynamic equations for nitrogen cycling within the model required the introduction of a soil organic matter compartment (aggregated in space and time) for each soil compartment being simulated. 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. Mineralisation in the model represents the net release of nitrogen that was formerly bound in organic matter, as  $\text{NH}_4^+$ . 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. 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  $\text{CN}_{\text{UP}}$  to  $\text{CN}_{\text{LO}}$ . 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.

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 at different points in the future. 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 the 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 and Gothenburg protocols 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.

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.

## **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**

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 long-term 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  $ANC_{crit} = 0$  and  $20 \mu\text{eq l}^{-1}$  using both the SSWC and FAB models. Exceedances of these critical loads have been calculated for the most recent national deposition dataset (mean 1995-97 values) and for a revised 2010 (post Gothenburg Protocol) deposition dataset which uses reduced N deposition generated by the FRAME model in conjunction with HARM modelled S and  $\text{NO}_x$  deposition (see NEG TAP Report).

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. 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  $\text{H}^+$ ) 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  $ANC_{crit} = 0 \mu\text{eq l}^{-1}$  assumes that a greater depression of ANC is acceptable (best case) than if  $ANC_{crit} = 20 \mu\text{eq l}^{-1}$  is used (worse case).

Under 1995-97 deposition levels, the percentage of sites exceeding their critical loads ranges from a best case of 16.6% (SSWC,  $ANC_{crit} = 0 \mu\text{eq l}^{-1}$ ) to a worst case of 29.7% (FAB,  $ANC_{crit} = 20 \mu\text{eq l}^{-1}$ ). Comparison of exceedances for both models using the same critical ANC ( $0 \mu\text{eq l}^{-1}$ ) shows the potential magnitude of the effect of increased nitrate leaching, 16.6% of sites according to the SSWC model (no increase in nitrate) and 25.2% of sites with the FAB model (major increase in nitrate leaching).

Similarly, assuming full implementation of the Gothenburg Protocol by 2010, its success can be assessed by reference to the proportion of freshwater mapping sites which remain exceeded. Using the same critical ANC ( $0 \mu\text{eq l}^{-1}$ ), the SSWC model indicates that only 7.3% of sites remain exceeded, while the FAB model suggests that 17.1% of sites still exceed their critical load. These figures increase if a higher critical ANC value is used. Note that these percentages apply only to mapping sites, selected to be the most sensitive to acidification, and are not applicable to the whole population of water bodies in the UK.

The Gothenburg Protocol should therefore succeed in significantly reducing the exceedance of freshwater critical loads in the UK, but is only partially successful in the complete prevention of acidification damage to surface waters.

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 modelled S and N deposition for the Gothenburg Protocol. With no modelled sulphur adsorption or 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.

## 2 RECOVERY

### Rationale

Following the stringent emissions reductions for sulphur which have already been implemented over the last 20 years and the planned reductions by 2010 under the Gothenburg Protocol, a major issue is now the assessment of how successful these policies will be in facilitating chemical and hence biological recovery, and over what timescales.

There are two aspects to understanding and modelling biological recovery. The first is the detection, prediction and modelling of chemical recovery. Detection of recovery can be achieved through trend analysis of long time series of water chemistry data, but these are sparse in the UK. Dynamic, process-based models (e.g. MAGIC) are generally used for the prediction of chemical recovery and the associated timescales. There are, however, still uncertainties associated with timescales of chemical recovery, due to hysteresis in certain catchment processes. The potential role of nitrate in curtailing chemical recovery is also important, and is discussed separately under Section 1.

Once confidence in measurements or predictions of chemical recovery has been established, the response of aquatic ecosystems needs to be understood. The measurement of biological recovery is complicated by the many potential confounding factors, for example the lack of complete chemical recovery, problems of biological recolonisation and the influences of other factors such as climatic variations (e.g. the North Atlantic Oscillation). Furthermore, the lack of data on post-acidification recovery because of the potential timescales involved has meant that experimental manipulations (e.g. liming) have often been the only way to test the biological effects of chemical recovery.

In addition to the above problems in measuring and modelling biological recovery, there is a separate issue of defining targets for recovery. The long history of acidification in parts of the UK has meant that there is a general lack of data on the original, pre-acidification chemical and biological status of acidified sites. With no historical data, alternative approaches have had to be developed for modelling pre-acidification, baseline conditions which can be used in the definition of appropriate recovery targets.

These research issues have been addressed in the current programme through the following approaches:

- Literature review and analysis of experimental data on the constraints and processes of biological recovery.
- Use of palaeolimnological techniques (analogue matching) to determine baseline conditions and hence potential chemical and biological targets for recovery.
- Analysis of existing long-term datasets for biology and chemistry to assess evidence for recovery..
- Application of dynamic and static critical load models to determine both rates of change and potential targets for water chemistry.

- Expansion of chemical-biological database for the development of predictive biological models.

The various tasks employed in these approaches are summarised separately below.

## 2.1 Continue monitoring for trends at the Galloway sites

Note that, as reported in the CLAM Mid-term Report, it was decided early in the project (after discussion with DETR) to focus resources on the Galloway region and redirect efforts and resources into new work on the effects of climate (North Atlantic Oscillation – see Section 2.7) and on extra coring and palaeolimnological analysis at two Galloway sites (described below). Extra sampling work at “exceedance study” sites initially proposed under this part of the work programme was abandoned in favour of these new priorities.

### 2.1.1 Chemical trends in Galloway

Studies of the ecological impacts of acidic deposition in upland areas of Galloway commenced in 1978 when 22 lochs and 27 streams were surveyed to provide fish population and chemical data. Chemical sampling progressed on a random basis prior to 1988 and thereafter on a monthly or three-monthly basis. A preliminary assessment of chemical trends for 5 high-elevation lochs between 1978 - 1994 (Harriman *et al.*, 1995) revealed a significant reduction in non-marine sulphate and an increase in pH and alkalinity. However, for Loch Grannoch, a lower elevation loch with a large proportion of coniferous forest in its catchment, there was no improvement in pH and Alkalinity despite a significant decline in non-marine sulphate.

Trends in chemical data were tested statistically using the Seasonal Kendall (SK) test which provided an estimate of the mean annual change and the significance of the trend. Supporting evidence for the significance of the trends was obtained using a randomised Linear Regression (LR) technique. At all sites for virtually all determinants any significant trend obtained using the SK test was matched by a significant LR trend.

17 sites were used in the analysis of the 1978-99 data (15 lochs and 2 streams) of which the catchments of 5 lochs (Riecawr, Macaterick, Grannoch, Harrow and Minnoch) and a stream (Green Burn) contain a large proportion of coniferous forest. Following a visual inspection of the data it became clear that the pattern of response to reduced S deposition was not linear but followed a more ‘stepped’ type of response. Consequently, trend analysis for 4 of the most sensitive sites was extended to cover the period 1988-98, to match the 10 year analysis of the AWMN data, and the 1995-1999 period to evaluate the most recent changes.

#### Trends for the 1978-99 period

For all sites, total  $\text{SO}_4^{2-}$  and non-marine  $\text{SO}_4^{2-}$  declined significantly ( $p < 0.05$ ) averaging 2.7 and 2.2  $\mu\text{eq l}^{-1}\text{yr}^{-1}$  respectively. There was a significant increase in pH at all sites (+0.015 pH units  $\text{yr}^{-1}$ ) while alkalinity increased significantly (+ 0.62  $\mu\text{eq l}^{-1}\text{yr}^{-1}$ ) except at the forested sites of Green Burn and Loch Grannoch.



Toxic forms of Al (Al-L) declined significantly at all sites but changes were greater at loch sites than stream sites. Conversely, non-toxic (organic) forms of Al (AL-NL) increased significantly, in line with increasing concentrations of dissolved organic carbon (DOC) which in many cases resulted in a non-significant change in Total Al.

Concentrations of  $\text{NO}_3^-$  showed a small but significant increase at loch sites but not for streams whereas the patterns of base cation change were extremely variable but with no overall trend. Marine salt (Na, Cl) concentrations varied considerably and although there was a slight downward trend over the period it was non-significant.

#### Trends for the 1988-98 period

Because the results of the above analysis differ, although not unexpectedly, from that of the Acid Waters Monitoring Network (AWMN) the data for the equivalent 10 year period were evaluated for four sites, three of which were also included in the AWMN (Grannoch, Round Loch of Glenhead and Dargall Lane). Fewer significant trends were obtained for this period and although non-marine  $\text{SO}_4^{2-}$  declined at three of the four sites only the Dargall Lane site showed a significant increase in both pH and alkalinity. In general, the rate of decline/ increase for most parameters was lower than the 1978-99 period while  $\text{NO}_3^-$  declined at Grannoch but increased at Enoch and Round Loch of Glenhead. Marine salt concentrations declined significantly at all sites except Grannoch where the decline was not significant.

#### Trends for the 1995-1999 period

The patterns of recovery for this most recent period indicate a faster rate of change but with some reversal of previous changes. For example, marine salt concentrations show a large and significant increase while  $\text{NO}_3^-$  concentrations declined significantly. This sharp decline in  $\text{NO}_3^-$  appears to be the result of especially high values in the 1995-97 period caused by increased N mobilisation following the long dry summers. Correspondingly high  $\text{SO}_4^{2-}$  concentrations were also recorded during the same period resulting in a significantly large decline in non-marine sulphate at all four sites. Only at Enoch and Round loch of Glenhead were significant increases in pH and alkalinity recorded whereas large reductions in Al-L were found at all sites, although the reduction at Dargall Lane was not significant.

It is evident from this assessment that the time-scale and start /end point of this time series has a major bearing on conclusions regarding recovery. Step-changes in the deposition pattern and climatic variations have directly influenced the recovery signal in these sensitive lochs and streams. Nevertheless, these waters are currently at their healthiest point of recovery since 1978.

#### *2.1.2 & 2.1.3 Biological trends in Galloway*

This report focusses primarily on evidence for the recovery of diatom populations in five acidified lochs (Loch Narroch, Round Loch of the Dungeon, Loch Grannoch, Round Loch of Glenhead and Loch Enoch), in the Galloway region of south-west Scotland, in response to reductions in sulphate deposition over the last two decades. Water chemistry monitoring has shown that all sites other than Loch Grannoch have undergone a recent amelioration in acidity.

Diatom analysis was carried out on sediment samples from annually sampled sediment traps (representing the last 10 years) and  $^{210}\text{Pb}$  dated sediment cores taken around 1990. Trap and core data were integrated, allowing high temporal resolution trends in diatom assemblages over the last decade to be examined in the context of the longer-term change. In a complementary study, new sediment cores were taken from Round Loch of Glenhead and Loch Enoch, and the most recent sediments extruded at 2 mm intervals and also subjected to diatom analysis.

Principal Component Analysis (PCA) of the integrated core-trap datasets showed that small species reversals had occurred at four of the lochs over the past two decades. Loch Grannoch, the only afforested loch, showed no reversal. A PCA of the top of the new sediment core from Round Loch of Glenhead also provided evidence of a recent species reversal, but this was not apparent in the new Loch Enoch core.

The direct gradient analysis approach of Canonical Correspondence Analysis, and the diatom-pH reconstruction method of Weighted Averaging Partial Least Squares (both based on the SWAP diatom-chemistry model), applied to the integrated core-trap datasets, demonstrated that recent species changes in Loch Narroch and the Round Loch of the Dungeon were strongly indicative of a response to declining acidity, providing clear evidence for biological recovery. In contrast the slight species changes identified by PCA at Round Loch of Glenhead and Loch Enoch could not be confidently attributed to a response to declining acidity. It is possible that these species reversals are as yet too small to translate as acidity responses according to the SWAP model, but it is also feasible that they represent a response to other environmental or biotic changes.

The findings of the analysis of the new sediment cores from Round Loch of Glenhead and Loch Enoch were in broad agreement with the core-trap study. A diatom pH reconstruction of the new Round Loch of Glenhead core provided tentative evidence for recent improvement, but the degree of change was well within the error estimates for the models. No recent rise in diatom inferred pH was detected in the new core from Loch Enoch.

Differences in the extent of recovery between sites may relate to catchment characteristics and sensitivity to climatic effects. The apparent continuation of acidification at Loch Grannoch is supported by recent water chemistry. This could result from a continued depletion of base-cations derived from a heavy application of rock-phosphate fertilizer as part of forestry management in the mid 1980s. The sediment trap assemblages of Round Loch of Glenhead and Loch Enoch show large inter-annual variability which could be driven by hydrological variation over the spring growing period. Inter-annual variability in spring chemistry may be large relative to any deposition driven improvement in water quality. Gradual recovery in the flora is therefore still expected but further years of monitoring are necessary before a clear response to declining acidity can be demonstrated.

An analysis of cladoceran remains in the new core from Loch Enoch revealed substantial changes in species and a drop in diversity over the period of acidification. This illustrates the wider ecological influences of acidification on these systems, and also demonstrates the broader potential of the sediment record for reconstructing and monitoring acidified ecosystems.

This report demonstrates the power of a combined sediment core – sediment trap approach for the assessment of recent biological change against a longer-term perspective. Similar approaches could be applied to other biological groups which leave fossil remains (including chironomids and cladocera) and would provide a more comprehensive assessment of the extent of ecosystem recovery in these chemically improving systems.

## **2.2 Run the MAGIC7 model on both a site-specific and regional mode**

### *2.2.1. Site Specific MAGIC 7 application to AWMN sites*

The MAGIC model was calibrated previously to the 22 sites in the UK AWMN in 1995 using the mean surface water chemistry from 1988 – 1994 to define the calibration targets and 1991 as the ‘present day’ reference year (Jenkins *et al.* 1997). The calibrated suite of models was used to assess the changes in surface water chemistry to 2041 in response to the Oslo Protocol. These calibrations have been updated where possible to a ‘present day’ reference year of 2000 and used to assess the changes in surface water chemistry in response to the Gothenburg Protocol. Best (MAGIC5) and worst (MAGIC7) cases of N retention are modelled although this is not possible at several sites since soil C/N data are not available. In addition, annual deposition fluxes have been calculated from adjacent deposition collectors in the ADMN and used to drive the model from 1988 – 1998 to enable comparison with the annual mean runoff chemistry from the AWMN and so providing an independent test of the model.

Catchment physical data, including soil chemistry and physical characteristics, were unchanged from the earlier calibrations. Forest management information, including felling and planting operations, was up-dated to 2000. At forested sites, future predictions assume felling of each stand at 50 years age and immediate replanting. Where possible, new soil samples were collected from the upper organic layers and analysed to estimate the C and N content.

Calibration of the model to ‘present day’ requires an estimate of mean annual chemistry. From the recent analysis of the AWMN chemistry data (Monteith and Evans, 2000), the recent trends towards decreased  $xSO_4$  preclude the use of mean data for the whole monitoring period as a calibration target. Consequently, the mean of the 1988 – 1993 period, when no significant trends were observed, was used for calibration. Wet deposition data for the same period was calculated from the nearest site in the ADMN and appropriate sea-salt and dry deposition factors were calculated for each site for  $Cl^-$  and  $SO_4^{2-}$ , respectively, on the basis of conservativity. Total deposition of  $NO_3^-$  and  $NH_4^+$  was derived from the UK 95-97 deposition data. The observed trend in wet deposition of  $xSO_4$  from 1990 was used to scale the deposition to 2000 (Smith *et al.*, 2000) for each site.

For model testing over the period 1988 – 1998, annual mean deposition chemistry from adjacent ADMN collectors was used. Annual rainfall totals from the ADMN gauges were used and evapotranspiration was calculated on the basis of percentage

mature forest cover in the catchment (moorland = 10%, mature forest = 25%) and assumed constant in each year.

Future forecasts were run for two scenarios; the Gothenburg Protocol and constant deposition at present level. Future deposition estimates for S and N for the Gothenburg Protocol were derived from HARM model outputs. In addition, two different model structures were used to describe future N dynamics. The best case assumes that the current retention of N will continue into the future as a proportion of input (MAGIC5). The worst case utilises a finite store of N within the soil and an empirical relationship to describe the proportion of N leakage in relation to the store size and the deposition flux (MAGIC7).

The calibrated model successfully matches mean 1988-1992 major ion chemistry and pH at all sites and there is no systematic bias in the calibrated determinands.

The pattern of change of ANC, pH and  $\text{SO}_4^{2-} + \text{NO}_3^-$  (the major acidic anions) through time at each site shows the historical build up of acid anions (SAA) in surface water to c.1970. At all sites except Loch Coire nan Arr and Allt a'Mharcaidh, this is predicted to have promoted some degree of surface water acidification. At Loch Coire nan Arr in NW Scotland, a site regarded as an un-acidified reference, no acidification is predicted to have occurred and reconstructed background ANC is well within the variation of presently observed values. Similarly, at Allt a'Mharcaidh in NE Scotland, simulated historical pH and ANC fall temporarily below the range of present day values but pH is not predicted to have been below 6.0. At these two sites, therefore, little change is predicted into the future.

Of the other sites, since the 1970s, all acidified sites are predicted to have recovered to some extent in response to a significant and rapid decline in SAA concentrations to present day. This decrease is in line with the 60% reduction in UK  $\text{SO}_2$  emissions since 1970 and the 70% reduction in European emissions. The extent of chemical recovery reflects the sensitivity of the site and the degree to which it was acidified.

Comparison of the model simulations against the observed annual runoff chemistry and using the observed annual deposition for 1988 – 1998 to drive the model gives generally good results. The range of variation in ANC and pH at most sites is generally well matched by the model. Continued testing of the model against observed time-series will promote increased reliability of model predictions.

Future predictions show an immediate increase in SAA under the constant deposition scenario. This results from the assumptions relating to N cycling within MAGIC7 i.e. the worst case whereby soil C/N is already  $\leq \text{CN}_{\text{UP}}$ . Under the deposition reductions associated with the Gothenburg Protocol, SAA declines to 2010 in both best and worst case models. Thereafter, in the worst case, N leaching increases whereas in the best case, N leaching remains constant into the future. The deviation in ANC between best and worst cases, therefore, is entirely the result of N leaching.

The time-series predictions must be interpreted with regard to the observed variation in annual mean chemistry. The model simulations into the future (beyond 1998) are driven by a 'smoothed' deposition trajectory and so do not reflect the variation in annual deposition that has been observed between 1988 and 1998. Since much of this

variation in annual deposition reflects changes in rainfall totals, it is likely that the ‘smoothed’ deposition reduction in the future will, in reality, reflect a similar variability. The relationship between variability in deposition flux and variability in mean surface water chemistry is unlikely to be linear but it is not currently known how the variation about the long-term mean will change as the sites recover from acidification.

The simulations for the whole suite of sites clearly demonstrate the benefit of the emission reductions in both S and N under the Gothenburg Protocol over making no further emission reductions. Under constant deposition and assuming the worst case of N leakage,  $\text{NO}_3^-$  concentrations increase while  $\text{SO}_4^{2-}$  concentrations remain stable. As a result, ANC and pH are further decreased at all sites.

Under the Gothenburg Protocol,  $\text{SO}_4^{2-}$  concentrations decrease significantly at all sites. This leads to a dramatic improvement in ANC which, as expected, is most marked at sites with the lowest ANC. The ‘best’ and ‘worst’ cases for N leaching, however, have a less significant impact on predicted ANC than the agreed S reductions. This is because  $\text{NO}_3^-$  concentrations at all sites are currently relatively low and even at a worst case assumption for decreased N immobilisation, the decrease in N is sufficient to keep the  $\text{NO}_3^-$  leaching at roughly its current level. This emphasises the importance of actually achieving the agreed S and N emission reductions to promote chemical recovery from acidification over the next 20 years.

### 2.2.2. Regional MAGIC 7 applications

Surface water chemistry data have been collected at a large number of sites in acid sensitive regions of the UK as part of this programme, as well as the CEH/MLURI Dynamic Modelling contract for DETR. The application of MAGIC 5 to five regions (Cairngorms, Galloway, Lake District, Dartmoor and Wales) and of MAGIC 7 to the South Pennines, is described in a report prepared under the Dynamic Modelling contract (Evans *et al.*, in press). This study was undertaken in order to assess the regional-scale impacts of different future deposition scenarios, and was based primarily on the simpler N dynamics of MAGIC 5, while MAGIC 7 has remained under development within the current programme.

Preliminary regional applications of MAGIC 7 have been undertaken for three regions where soil C and N data were also available; Galloway, the South Pennines and Wales (Section 1.5.1). Modelling procedures were the same as those described in the preceding section, except that calibration was based on a single spring sample (South Pennines, Galloway) or one year of monthly samples (Wales). Future changes in surface water chemistry have been modelled using HARM deposition forecasts for the Second Sulphur Protocol (‘Reference Scenario’).

Results of these simulations show marked variability between regions. In the most highly impacted South Pennine region, 24 of the 58 calibrated sites currently have a negative ANC, but with the large  $\text{SO}_4^{2-}$  reductions forecast under the Reference Scenario, this is predicted to reduce to 10 sites. However,  $\text{NO}_3^-$  concentrations, which are already high in the region (median  $41 \mu\text{eq l}^{-1}$ ) are predicted to rise significantly, exceeding  $60 \mu\text{eq l}^{-1}$  at 35 sites by 2050. These  $\text{NO}_3^-$  increases will thus significantly

offset recovery due to falling  $\text{SO}_4^{2-}$ , and in the longer term, as N leaching increases further, lead to some re-acidification.

In Wales, although acidification is less severe than in the South Pennines, many sites throughout the study region currently have low or negative ANC. By 2050, it is predicted that almost all sites will have a positive ANC, with low-ANC ( $< 25 \mu\text{eq l}^{-1}$ ) streams largely restricted to central Wales. In contrast to the South Pennines,  $\text{NO}_3^-$  currently makes a relatively minor contribution to stream acidity, and this situation is not predicted to change markedly, with most streams retaining concentrations below  $20 \mu\text{eq l}^{-1}$  in 2050.

The situation in Galloway is fairly similar to that in Wales; acidic conditions are currently observed in the central part of the region, whilst  $\text{NO}_3^-$  concentrations are low to moderate. Forecasts suggest substantial recovery by 2045, with a halving of the number of lochs with a negative ANC. Again, this recovery is driven mainly by reductions in  $\text{SO}_4^{2-}$ , with relatively minor changes in  $\text{NO}_3^-$  concentrations.

### **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 disturbances**

#### Large-scale long-term issues in the recovery of ecosystems from acidification.

1. In the UK, the effects of acidification have been unique in combining impacts on ecosystems that are both large-scale and long-term: large contiguous upland areas are assumed to have changed over time periods that exceed decades-centuries. Indications from theory and observation indicate that effects of this type require proportionately long time scales for recovery (i.e. decades-centuries). Indeed, the scales involved are greater than in many previous ecosystem disturbances (e.g. extraction industry; deforestation) so that the knowledge required to forecast both the extent and time required for true recovery is scarce.
2. Available theory and observation from other disturbances suggest that either of i) ecosystem structures (e.g. diversity, community composition) or ii) ecosystem functions (e.g. production, decomposition, predator-prey interactions) might not return to pre-disturbance conditions within practically measurable timescales. At best, therefore, “recovery” should be considered as damage reversal towards some target endpoint rather than true repair or restoration.
3. Endpoints from which recovery has been judged in the past are overwhelmingly structural (community composition; the presence and absence of key species). Functional indicators are used less commonly. Since we still know less of the effects of acidification on ecosystem processes in rivers, so too our understanding of the functional indicators of recovery is weak.
4. The particular characteristics of catchment, river and lake ecosystems provide several points at which there might be lag effects on recovery processes. In catchments, this includes the factors required to return base-cation distribution within

the soil profile and hydrological pathway to those pertaining before acidification. In aquatic systems, it includes:

- 4.1 The removal of pulsed disturbances that might offset recovery, such as acid episodes;
  - 4.2 Organism dispersal within or between the naturally fragmented units that make up lakes and rivers;
  - 4.3 The need for recovery to pervade whole food webs from the smallest organisms to the largest so that functional integrity is restored;
  - 4.4 The intrinsic limits on population rates of recovery;
  - 4.5 The need for environmentally sensitive management that prevents interference from other ecosystems stressors on both physico-chemical and biological recovery.
5. Should forecasts and rates of change due to deposition reduction be limited or slow, interventionist management is likely to be considered by some agencies. Artificial intervention is possible within catchments (i.e. liming), and at stages 4.1-4.2 (species re-introductions) and 4.5 (e.g. agri-environment schemes that deliver sensitive catchment management; wider environmental protection that offsets climate change). None of these measures is without constraints and uncertainties.
6. The Water Framework Directive is likely to drive targets and prescriptions that require us to establish reference conditions for surface waters prior to acidification. It will also require management strategies that promote recovery. A range of uncertainties currently affect our abilities in this regard.

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

Under this part of the work programme, a comprehensive desk study was produced and submitted to DETR in Year 2 of the contract (Simpson, 2000). The key points from the desk study are summarised below.

- 1) 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.
- 2) Most of these palaeolimnological applications have been based on diatom analysis, and the use of diatom-pH transfer functions to make reconstructions of hydrochemical change in upland lakes associated with acidification.
- 3) 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.

- 4) 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.
- 5) 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.
- 6) 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 data set used to identify modern analogues contains the range of hydrochemical conditions represented by the fossil assemblages;
  - c) that a suitable stable 'baseline' (pre-impact) status can be defined.
- 7) Prior to more comprehensive application of the modern analogue approach to acidified lakes in Britain, these assumptions require evaluation. Three studies are proposed:
  - 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 cladocera) 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.

These recommendations fed into the development of the work programme under Section 2.5 below.



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

Recovery in acidified upland lakes is the focus of much of the current work on lake acidification. Measuring and modelling recovery in the light of emission reduction protocols are important in evaluating the effectiveness of pollution abatement strategies. Evaluating recovery of acidified lakes towards a target based on their pre-acidification status is a more difficult task as there are very few biological records for these remote upland systems. The analogue matching approach can be used to identify modern analogues for the pre-acidification status of lakes using the sub-fossil remains of the diatoms and the cladocera; these analogues can then be used in the formulation of recovery targets.

An 83-lake modern training set was created, with full diatom, cladoceran, water chemistry and catchment data for each lake, selected to reflect the range of likely conditions found in upland systems in the 1800s. Fossil samples from 8 AWMN lakes were chosen to represent pre-acidification conditions in those lakes, and the closest analogues in the modern training set were identified by means of the squared chord distance measure.

Close modern analogues were identified for 7 of the 8 AWMN lakes. The majority of these modern analogues are located in North and Northwest Scotland; areas of low sulphur and nitrogen deposition. Comparison of the chemistry and catchment characteristics of the AWMN lakes to those of the modern analogues showed that the modern analogues had higher lake water pH and alkalinity levels and lower aluminium concentrations. Ionic strength and calcium concentrations in the modern analogue lakes were also very similar to observed values in the AWMN lakes.

These results indicate that the analogue matching approach using diatom and cladoceran remains is a simple, robust and reliable method of identifying modern analogues for acidified lakes in upland areas of the UK. The modern analogues provide suitable reference conditions for pristine upland lake ecosystems and may be used to evaluate progress made towards restoration in acidified lakes.

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

A combined database has been constructed using existing and new datasets to provide information on diatom, macrophyte and invertebrate distribution in relation to a range of water chemistry variables for 459 samples. This new database greatly expands the number of taxa and range of chemical gradients available in previous individual datasets. As such the new database captures taxon distributions more fully and allows modelling along the full range of taxon distribution along multiple chemical gradients.

Community ordination analysis using detrended correspondence analysis (DCA) and canonical correspondence analysis (CCA) indicates that the subset of chemical variables available for all samples (pH, alkalinity, conductivity,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and

total monomeric aluminium) effectively account for the dominant biological gradients in the diatom and invertebrate datasets.

Logistic regression response models fitted to individual diatom and invertebrate taxa with 20 or more occurrences indicate that all 50 selected diatom taxa, and 31 of 39 selected invertebrate taxa, show statistically significant responses to pH. These results are used to identify potential indicator taxa with varying degrees of tolerance to lowered pH. Although there is a statistically significant relationship between macrophyte community composition and pH, the macrophyte dataset is at present too small (28 sites) to allow the modelling of individual taxa.

Predictive models are derived for three biological targets, the diatom *Achnanthes minutissima*, the invertebrate *Baetis rhodani* and an acid tolerant diatom assemblage. *Achnanthes minutissima* and *Baetis rhodani* are both common in streams above pH 6.0, and are among the first taxa to decline in response to lowered pH. The acid tolerant diatom group is characterised by *Eunotia exigua*, an acidobiontic taxon commonly found in acidified waters.

The fitted logistic regression models can predict the occurrence of the target organisms with an internal success rate of c. 70%, and provide a means of predicting the probability of occurrence of the target organisms from modelled hindcasts and forecasts.

Application of the models to the CLAM national chemical database using the SSWC model provides biological predictions for baseline (pre-acidification), present, and future (Gothenburg scenario) conditions. Comparisons of the mapped biological predictions for baseline and present indicate substantial biological change in the areas of known acidification: SW England, Wales, Cumbria, Pennines and large parts of Scotland. The loss of sensitive taxa predicted for sites in the north of Scotland are probably the result of errors in the calculation of non-marine ANC for sites with high inputs of sea-salt. Comparison of predictions for baseline and future steady state ANC suggest virtually complete biological recovery under the Gothenburg scenario.

Biological predictions for five MAGIC 5 regions (Cairngorms, Galloway, Pennines, Wales, Lake District) show similar patterns of biological change between baseline and present, with loss of sensitive taxa from 18% of sites in the Cairngorms through to loss from 60% of sites in the Pennines. Predictions for recovery under the Gothenburg scenario indicate that only partial recovery will take place by 2050, and for some regions sensitive taxa are predicted only to return to approximately half of the sites inhabited prior to the onset of acidification.

The biological models provide a simple but robust way to convert hydrochemical hindcasts and forecasts into measures of biological change, and in particular, to assess biological damage under different emission reduction scenarios. However, there is a need to validate the models using independent field data, and a need to reconcile the differences in hydrochemical predictions between the SSWC model and MAGIC 5.

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

### 2.7.1 Hysteresis

Work carried out on hysteresis in biological recovery, funded by DETR and other agencies, is described in the manuscript “Assessing hysteresis in biological response to chemical recovery from acidification: the case of limed streams at Llyn Brianne” (D.C. Bradley and S.J.Ormerod, submitted for publication). The work is summarised below.

There is a need to assess the factors that might delay biological recovery in streams recovering from acidification, but real chemical recovery has so far been insufficient to satisfy this need. However, catchment liming causes accelerated deacidification and provides an opportunity to assess the speed of accompanying biological response. Using the replicated basin-scale experiment at Llyn Brianne, we assessed chemical and biological effects for 10 years after the catchments of three acidified Welsh streams were limed in 1987/88.

Stream chemistry was measured weekly to monthly, and macroinvertebrates monitored annually, between 1985 and 1998. Biological change through time was assessed from the abundance and taxon richness of invertebrates. We paid particular attention to 18 species known to be acid-sensitive. The effects of liming were assessed by comparing chemical and biological trends among the three replicate limed streams, three acid reference streams and two naturally circumneutral streams.

Following single lime applications, acid-base chemistry in treated streams changed significantly. High mean pH ( $> 6$ ), increased calcium ( $> 2.5 \text{ mg l}^{-1}$ ) and low aluminium ( $< 0.1 \text{ mg l}^{-1}$ ) persisted throughout the 10 years following liming.

The effects of liming on invertebrates were modest. Acid sensitive taxa increased significantly in abundance in limed streams, but only during 2 years following treatment. Significant effects on richness were more sustained, but on average added only 2-3 acid-sensitive species to the treated streams, roughly one-third of their average richness in adjacent circumneutral streams. Only the mayfly *Baetis rhodani* and the stonefly *Brachyptera risi* occurred significantly more often in limed streams after treatment than before it.

Despite these modest effects on invertebrates, nearly 80% of the total pool of acid-sensitive species has occurred at least once in the limed streams in the 10 years since treatment. This pattern of occurrence suggests that the delayed colonisation of limed streams by acid-sensitive taxa reflects limited persistence rather than restricted dispersal. We present evidence to show that episodes of low pH continued to affect acid-sensitive taxa even after liming. At Llyn Brianne, hysteresis in streams recovering from acidification is real, but might reflect the continued effects of episodes rather than other biological limits.

### 2.7.2 Stochasticity

Work carried out on stochasticity (funded by DETR and other agencies), as influenced by climatic patterns, is described in the manuscript “Evaluating variations in invertebrate communities in upland Welsh streams: persistence tracks the North Atlantic Oscillation” (D.C. Bradley and S.J.Ormerod, submitted for publication). The work is summarised below.

This work began as an evaluation of apparently stochastic variations through time in invertebrate communities in upland Welsh streams. Large variations between years in the persistence (= constancy) of invertebrate communities was apparent during the Welsh Acid Waters Survey, and was seen as a factor that might confound or obscure other trends. As a result of further work, these apparently stochastic variations are now understandable.

The North Atlantic Oscillation (NAO) affects marine ecosystems, lakes and some terrestrial ecosystems around the Atlantic rim, but evidence for effects on rivers is scarce. For 14 years, we sampled riverine macroinvertebrates in 8 independent streams from the Llyn Brianne experimental catchments in central Wales. We assessed whether year-to-year persistence in rank abundance and species composition tracked the NAO.

Persistence was quasi-cyclical and varied synchronously across all streams irrespective of chemistry and catchment land use. Invertebrate communities in all stream types or habitats switched significantly from being highly persistent during negative phases of the NAO (winter index  $<1$  = cold, dry winters) to unstable during positive phases ( $>1$  = mild, wet winters). These effects occurred in both rare and common taxa.

Acid episodes could not explain low persistence in positive NAO years because variations in acid-base status were not linked to the NAO. Moreover, fluctuations in persistence were apparent even in well-buffered streams.

Discharge in adjacent gauged catchments increased in positive NAO years by 15-18% but neither flow variability nor flow maxima were higher. Nor were variations in invertebrate persistence at Llyn Brianne directly correlated with discharge pattern. Discharge variations alone were therefore insufficient to explain links between persistence and the NAO, but we cannot exclude subtle effects due either to flow or temperature.

These data illustrate how the persistence of invertebrate communities at Llyn Brianne is not entirely stochastic, instead varying with environmental fluctuations. Positive phases of the NAO are accompanied by ecological instability in the Llyn Brianne streams, although the exact mechanisms are currently unclear. The effects of the NAO might confound or obscure other long-term change in rivers such as recovery from acidification or the effects of global warming, unless accounted for in monitoring programmes. These patterns, if increase in the amplitude of the NAO continues, might cause further instability in aquatic habitats.

### 2.7.3 Episodicity

Work carried out on episodicity, funded by DETR and other agencies, is described in the manuscript “Parameterising and modelling the ecological effects of acid episodes” (D.C. Bradley and S.J.Ormerod, in preparation for publication). The work is summarised below.

Episodic fluctuations in pH and associated stream chemistry occur in acid-sensitive surface waters and are widely assumed to be important biologically. However, assessing and modelling their ecological effects has presented considerable difficulty since standard measures of episodicity are often correlated with and subsumed within the measurement of mean chemistry.

Using regional data from 70 independent streams in Wales, we examined i) whether modal values for pH and Al concentration better described base-flow chemistry from which episodic departures could then be assessed; ii) whether these episodic departures reflected biological status; iii) whether regression models for predicting invertebrate abundance, taxon richness and trout density were improved significantly by measures that separated episodic departures from modal chemistry and iv) whether model performance improved when applied to independent test sites.

Chemical data revealed three site groups respectively characterised by high modal pH (>6) with pronounced episodes; high modal pH (> 6) but no episodes; and chronic acidity (modal pH <6). Invertebrate abundances, taxon richness and trout densities did not differ significantly between episodic and chronically acidic sites. By contrast, there were clear differences between episodic and stable sites despite similarly high modal pH, particularly among acid-sensitive invertebrates.

Indices of pH and Al episodicity significantly improved regression models that predicted biological status over models based on modal values alone. Models based on modal pH and mode – minimum pH accounted for the most variation in the faunal communities. At test sites, invertebrate abundance, taxon richness and trout density predicted by models using episodic chemistry generally correlated with actual biological status, but there was evidence of systematic over-prediction at acid sites and under-prediction at sites with higher pH.

These data show that measures of episodicity that reflect departures from modal chemistry reflect what appear to be the biological effects of acid episodes. Nevertheless, models of complex interactions between variable stream chemistry and stream biota presents further challenges.

## **2.8 Develop linked hydrochemical-biological models to predict biological outcomes from MAGIC-WAND and other dynamic models**

See Section 2.6 above.

## **2.9 Run the MAGIC7 model for different afforestation strategies**

MAGIC 7 simulations have been carried out under different forestry scenarios for the Galloway dataset. Thirty six of the sixty catchments in this region 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. The model predicts an increase in ANC at all moorland sites, whereas, despite the emission reductions, several forested sites undergo a further deterioration in ANC, albeit relatively small. The predictions indicate that plantation forestry should be avoided in areas that are sensitive to acidification.

Despite emission reductions, soil base saturation (BS) is predicted to decline from 1997 to 2047 for the majority of catchments in the region. 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.

## **2.10 Organize a workshop with environmental economists to ensure cost-benefit modellers are well informed of the relevant science output**

A workshop was organised by DETR to scope out methods for economic assessment of ecosystems, and a presentation was made on the scientific information on impacts of acidification on freshwaters by scientists under this contract. Rick Battarbee, Alan Jenkins and Don Monteith attended the workshop. Separate reports of this workshop have been produced outside this contract.

## 3 HEAVY METALS

### 3.1 Scoping study

The aim of this study was to collate information with respect to atmospheric deposition of metals to freshwaters across the UK with an emphasis on temporal and spatial trends, monitoring and the potential for setting critical loads.

#### 3.1.1 Emissions

Anthropogenic emissions of heavy metals in Europe have been much reduced since the early 1970s (e.g. cadmium (Cd) 40%; lead (Pb) 39%; zinc (Zn) 32%). Reductions are due to the introduction of more stringent controls on emissions, advances in technological processes and, for Pb, removal from petrol. Although the UK is a net exporter of atmospherically-transported metals it is the biggest single receiver of UK emissions. However, uncertainties in the calculation of emission estimates are significant for Pb, Cd and mercury (Hg).

#### 3.1.2 UK deposition monitoring

Decreasing trends in emissions have been identified most clearly in the UK's longest running metal monitoring programme, the Rural Network. Concentrations in chromium (Cr), nickel (Ni) copper (Cu), arsenic (As), vanadium (V), Zn and Pb deposition decreased by 3 - 11% per year between 1972 - 1991. There has also been a reduction in deposition to urban areas since 1976 identified by the Multi-Element Network. Pb has shown the most consistent decreases with a 9 - 18% per year reduction. Largest Pb decreases are seen post-1986/7 associated with the reduction of lead in petrol. The Rural and North Sea Networks provide high resolution data for rural areas but the number of sites are too few to enable accurate national deposition maps to be made. Atmospheric transport and deposition in the UK are heavily influenced by meteorological conditions and assessment of depositional trends must take these into account. Similarly, future climate change could potentially have a major impact on inputs to freshwaters, particularly with respect to the release of catchment stored metals.

#### 3.1.3 Methods of assessing metal deposition trends by other than direct means.

- Terrestrial mosses (esp. *Hylocomium splendens* and *Pleurozium schreberi*) are widely used as biomonitors of atmospheric metal deposition. Moss monitoring surveys in the UK have identified the English midlands and the north of England as areas of highest deposition.
- Sediment trap samples provide a means by which accurate time periods of metal deposition to lake systems can be monitored relatively easily, even in remote locations.
- Dated lake sediments have been widely used for assessing temporal trends of past metal inputs. Upland and remote lakes offer the opportunity to study metal contamination as it is usually entirely atmospheric in origin.
- Analysis of standing waters can offer high resolution data. However, use of surface waters as a means of determining atmospheric deposition concentrations is complicated by retention and interaction of soils and vegetation.

#### 3.1.4 Critical loads

Legislative controls on atmospheric emissions of Cd, Hg and Pb have been outlined in the Heavy Metals Protocol (1998) and the EC proposes to further this by setting air quality standards for As, Cd, Hg and Ni in a forthcoming Air Quality Daughter Directive. Although emissions have been reduced significantly there is still much debate over what constitutes a 'safe' level in terms of human and environmental health. To this end, the critical loads approach is now being developed. The definition of critical loads for metals will be essential in "preventing and reducing harmful effects on (human health and) the environment as a whole" (EC Air Quality Framework Directive )(96/62/EC). However, there is still much to be done, including:

- provision of a unified critical loads methodology which is applicable at a national (and regional) level in upland and lowland areas;
- selection of suitable receptor organisms and setting of critical limits; and
- collection of suitable model input data and selection of a model.

### 3.2 Metal deposition and cycling at Lochnagar

The aim of this part of CLAM project was to continue the metals research programme at Lochnagar in order to provide:

- an assessment of the role that catchment and lake biota and sediment trapping can play in the monitoring of metal deposition and/or lake water metal concentrations with a view to future monitoring at a larger number of sites;
- an indication of any temporal trends that might become apparent; and
- data on mercury, sparse within the UK, in the various ecological compartments at an upland lake site.

Meteorological data and lake water temperature at a number of depths were monitored automatically throughout the period by means of an Automatic Weather Station sited on the loch shore and a thermistor chain located in the deepest part of the loch basin.

Trace metals, principally mercury (Hg), lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni) and zinc (Zn), were measured in lake waters and bulk deposition every two weeks. The metals were also measured in annually collected samples of terrestrial and aquatic plants, epilithic diatoms, zooplankton and shallow and deep water sediment traps.

Hg data suggest that atmospheric deposition has increased over the last three years. However, a longer dataset is needed to follow, and confirm, this trend. Hg deposition concentrations are greater than their equivalent lake water concentrations and this suggests that Hg is bound and stored in catchment soils. This is supported by other studies and implies that there is a massive store of Hg and other trace metals in the catchment soils which could be released if soil erosion were to continue to increase as a result of, for example, future climate change.

The other metals show a decline in deposition, and all except Pb show a decline in lake water concentrations. V and Cu, like Hg, show deposition concentrations greater than lake water concentrations most of the time. However, all metals have higher concentrations in lake water than deposition during the winter period November 1999



– February 2000. The reason for this is currently unclear, but may be due to wind directions from a more northerly (less polluted) direction during the winter.

Most terrestrial plant species followed similar decreasing trends to those of atmospheric deposition, suggesting possibilities as a monitoring tool. *Hylocomium splendens* and *Pleurozium schreberi*, widely and inter-changeably used in metals monitoring programmes, generally showed good agreement with atmospheric trends and with each other. However, reeds and grasses (e.g. *Nardus stricta* and *Juncus* sp.) showed poor agreement with atmospheric deposition trends.

Aquatic plants showed less agreement with depositional trends and generally showed no trend or an increase over the period. This may be due to increased inputs from the catchment. Epilithic diatoms on artificial substrates showed limited usefulness primarily due to the low amounts of material produced. They may be more useful at more productive sites. Sediment traps show very good potential for monitoring lake metal trends and suggest catchment inputs may be very important.

Some trends have been observed, but longer periods are required. Monitoring needs to be undertaken at other upland sites to confirm Lochnagar results. This is particularly important in NW Scotland, which could act as a reference site for contemporary UK deposition.

Ongoing and extended spatial monitoring is particularly important for Hg, as there are so few UK data.