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**Critical Loads in Freshwater Ecosystems (1995-1998): A
Summary Report to the Department of the Environment,
Transport and the Regions**

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INTRODUCTION

This report summarises the results of the three year research programme "Critical Loads in Freshwater Ecosystems (1995-1998)" funded by the Department of the Environment, Transport and the Regions. The detailed results are presented in 26 separate paper and reports (see listing below). The current report summarises the outcomes of the research with specific reference to individual work units within the overall work programme.

The research programme has made the following key achievements:

- (1) the development of a high-quality national chemical database for model validation and national critical loads mapping;
- (2) the development and application of the first-order acidity balance (FAB) model for national critical loads mapping;
- (3) the development of a dynamic modelling capability at a range of spatial scales from headwater catchments to the whole UK using the MAGIC, MAGIC-WAND and MAGIC7 models. This dynamic modelling approach offers key evidence on the timing of recovery in response to emission reductions, and provides the capability to consider other factors such as land use and climate change;
- (4) the production of new assessments of freshwater acidification in the UK using the FAB and MAGIC-WAND models;
- (5) the further development of high quality chemistry-biology datasets and the associated developments in biological modelling;
- (6) the development and application of new approaches for identifying restoration targets for acidified ecosystems using the palaeolimnological record;
- (7) the establishment of strong working links and collaboration within the freshwaters critical loads group;
- (8) the organisation of two international workshops on key themes relating to critical loads in freshwater ecosystems - the role of nitrogen (11th September 1997) and the prospects for recovery (9th January 1998).

Specific achievements in relation to the individual work units of the programme are detailed below.

NITROGEN

1.1 Development of critical loads models to incorporate N deposition

1.1.1 The empirical steady-state water chemistry (SSWC) model has been developed to become a model for total acidity (S + N) by including measured surface water nitrate in the F factor needed to calculate the critical load, and by using the total acid anion method for exceedance calculations (Harriman *et al.* 1995a).

1.1.2 The empirical diatom model (Battarbee *et al.* 1996) has been modified for calculating critical loads and exceedance based on total acidity. The re-calibration and application of the model is described by Allott *et al.* (1995a).

1.1.3 The first-order acidity balance (FAB) model has been implemented using the CLAG chemistry ACCESS database. The implementation and development of the model for UK application is described by Curtis *et al.* (1998a). The model represents a simple mass- and charge-balance incorporating the major sources and sinks of S & N. The model includes terms for N uptake, N immobilization, denitrification and in-lake N retention. The model uses water chemistry data available from field survey and catchment data obtained using a geographical information system (GIS).

1.1.4 The MAGIC model has been extended (MAGIC-WAND) to replace the previous simplified description of N dynamics as a percentage retention of input at each timestep with a full mass balance of N incorporating the key N processes (Ferrier *et al.* 1995; Jenkins & Renshaw 1995). The processes included are nitrification, mineralisation/immobilisation, plant uptake and denitrification. Since field measurements of these fluxes are scarce, however, the model has been further simplified (MAGIC7) whereby immobilisation/ mineralisation is determined with respect to C availability. The model utilises data which can be easily collected in the field and initial tests indicate that these main processes are capable of describing observed stream N concentrations across a range of sites. This model can now be used to assess the impact of coupled S and N emission reduction scenarios on surface waters at site and regional scale across the UK.

1.2 Model validation

The CLAG Nitrogen Network was set up to provide the data required to thoroughly test the freshwater critical loads models for sulphur and, more specifically, nitrogen (Curtis 1998b). The FAB and MAGIC7 models require data on the rates of several catchment processes, mostly involving nitrogen cycling and removal, and on a national basis these data have to be obtained from estimates for each soil or land cover type in the scientific literature. A primary function of the Nitrogen Network was to facilitate the testing of model assumptions and performance at a number of intensively monitored sites.

The network of 13 sites covers the important gradients of N deposition load and site sensitivity. Digital catchment outlines were overlain on to national datasets to obtain catchment estimates of annual runoff, S and N deposition, land and soil cover. Seasonal variability in water chemistry and catchment output fluxes were studied by

monthly water sampling from the selected inflow stream and the lake outflow. The seasonal patterns of chemical variation are described by Curtis *et al.* (1998b). The dataset has been used for model development (Curtis *et al.* 1998a; Harriman *et al.* 1998) and validation (Curtis *et al.* 1998a).

The network has also been supplemented for data analysis using a dataset of nitrogen leaching from large Scottish lochs (Harriman 1998a). These data have also been used in model development (Harriman *et al.* 1998).

To parameterize the FAB and MAGIC models for national applications a major catchment digitizing programme was undertaken. The geographical information system ARC/INFO was used to quantify soil cover, land cover and lake to catchment ratios for catchments in the CLAG database of UK water chemistry. The digital catchment boundaries were exported to ITE Monks Wood and overlaid onto the digital land cover map of Great Britain to obtain the percentage of each land cover type in each catchment. This has enabled the forest coverage in each catchment to be estimated. To obtain the soils data required for FAB and MAGIC, digital catchments were exported to SSLRC (English and Welsh sites) and MLURI (Scottish sites). For MAGIC a value for each required soil parameter was derived for each soil series/association present throughout the catchment database by averaging values found in profile databases. Initially, horizon values were converted into single values for the profile, weighted according to horizon thickness. Each parameter was then weighted spatially on a catchment basis according to the areal coverage of each soil series. For the FAB model the percentage of each soil type in each catchment was determined so that catchment weighted immobilization and denitrification values could be calculated.

The applications of these models at the national level using these data are described below.

A direct comparison of critical load methods for soils and freshwaters at headwater catchment scale (Jenkins *et al.* 1997a) indicates a great variation between the approaches. The results indicate that the freshwater critical load calculations fall within a wide range of soil critical loads for the same sites. The need to consider the time to recovery emphasises the need to use dynamic models although data requirement tends to be higher.

1.3 Spatial variability of nitrate concentration

The spatial variability of nitrate concentrations in upland waters was evaluated at a national scale by Allott *et al.* (1995b) using the CLAG chemistry dataset. This study highlighted elevated concentrations of nitrate in Wales, the Pennines, Cumbria, Galloway and the Cairngorms and demonstrated a clear relationship between surface water nitrate and total N deposition. However, significant differences in the patterns of surface water nitrate concentration were observed within areas of similar N deposition. The high deposition Snowdonia area of North Wales was chosen for further study to assess regional variation in nitrate concentrations and to identify catchments vulnerable to nitrate leaching (Kernan & Allott 1998). It was decided to focus on a single study area rather than two in order to allow seasonal variation in nitrate concentrations to be evaluated. The study highlighted the variability in nitrate levels within the study area,

primarily due to variations in catchment specific processes . However, nitrate makes a significant contribution to freshwater acidity, particularly during winter, and nitrate breakthrough has occurred at many of the study sites. The highest leaching levels both in winter and summer occur in catchments where soil and vegetation cover is limited. Nitrogen cycling in these generally high altitude catchments may no longer be governed by seasonal biological controls, and these catchments are likely to be saturated with respect to nitrogen as a result of the elevated deposition levels in the area. The study empirically demonstrates the importance of catchment factors in modifying the relationship between N deposition and N leaching in upland catchments.

1.4 Assess suitability of the current site database for N critical loads

The suitability of the sites in the CLAG chemistry database for calculating and mapping N critical loads at a national scale was evaluated by desk study at the start of the project. Where necessary, new sites were sampled.

1.5 Production of new critical load exceedance maps

Critical load exceedance maps for total acidity using the empirical models are presented by Allott *et al.* (1995a) and Harriman *et al.* 1995a). However, these approaches cannot be used for scenario testing as they are formulated using current nitrogen leaching . The work programme therefore concentrated on the production of critical load exceedance maps using the FAB model (Curtis *et al.* 1998c, 1998d).

Curtis *et al.* (1998c) present critical loads maps using the FAB model for current measured deposition. The model predicts that when catchment processes reach steady-state with these deposition levels, increases in nitrate leaching will depress acid neutralizing capacity (ANC) below the critical threshold of $0 \mu\text{eq l}^{-1}$ at more than a quarter of the sites sampled (i.e. the critical load is exceeded at these sites). There is regional variation in the deposition requirements for protection of the sampled sites. The FAB model predicts that in Scotland most of the sampled sites could be protected by sufficiently large reductions in S deposition alone. In the English and Welsh uplands, both S and N deposition must be reduced in order to protect the sites.

Curtis *et al.* (1998d) apply the FAB model to the CLAG national freshwaters dataset using three deposition scenarios using the Hull Acid Rain Model (HARM). This includes a scenario representing the planned emissions reductions under existing international commitments (REF scenario). The Model predicts that the planned reductions in emissions under the REF scenario will protect most Scottish freshwaters, but that substantial numbers of sites in the English and Welsh uplands will remain exceeded.

However, there are significant uncertainties associated with application of the FAB model. Firstly, there are uncertainties associated with the parameterization of the model, and the reliability of the default terms used to represent nitrogen sinks (Curtis *et al.* 1999a, 1998d). These uncertainties will be specifically addressed in the new work programme. Secondly, the FAB model assumes steady-state conditions and provides

no data on the timing of chemical change or recovery. This issue has been addressed by the use of dynamic models (see below).

1.6 Co-ordinated regional lake survey

Random chemical surveys of lakes in Wales and Scotland were undertaken in 1995 as part of the co-ordinated Northern European Lake Survey (Henriksen *et al.* 1998). These data allow comparison of water chemistry and critical loads across north-west Europe (Henriksen *et al.* 1998). Critical loads for sulphur were calculated using the modified SSWC model with a variable ANC limit. Critical load values for the Scottish and Welsh lakes were relatively high in comparison to Fennoscandian lakes.

1.7 Biological response to increased N in surface waters (I)

The CLAG chemistry-biology database has been expanded and further developed (see below) (Juggins 1998), and this has allowed the biological response to increased nitrate concentrations in upland surface waters to be explored. Allott & Kreiser (1998) used multi-variate statistics to test the hypothesis that there is a significant relationship between nitrate levels and diatom populations. Diatoms are key primary producers in upland freshwater ecosystems and form an important test group for these relationships. The study demonstrated a significant relationship between nitrate concentrations and diatom assemblages, independent from the relationship with acidity. This suggests that elevated nitrate levels in upland surface waters can cause structural changes in diatom assemblages which are unrelated to the effect of acidity alone. This is a significant finding, and similar relationships with other biological groups will be evaluated in the new work programme.

1.8 Biological response to increased N in surface waters (II)

The original work programme included a lake manipulation experiment on the proviso that resources allowed such work to proceed. After discussions in the first year of the programme, and a desk review of the likely costs of such an experiment, this study was abandoned due to cost constraints. Resources were re-employed for the catchment digitisation programme.

1.9 Contribution of N deposition to nutrient concentrations in lowland catchments

It is often assumed that high levels of nitrate in lowland waters are exclusively derived from sewage and agricultural sources of N, and that atmospheric N sources play a negligible role. The potential contribution of nitrogen deposition to nitrate fluxes from lowland grassland catchments was studied by reference to a dataset from 30 Welsh lake catchments. These lakes provide a gradation from upland oligotrophic systems to high alkalinity, nutrient rich lakes in the lowlands. Nitrogen budgets were constructed for these catchments and nitrogen deposition fluxes compared to catchment nitrate fluxes. In all catchments but one, nitrogen deposition fluxes were greater than catchment nitrate fluxes. Although these lake catchments have relatively low nitrate levels compared to other lowland systems, the study demonstrates the potentially important role of nitrate deposition in the nutrient budgets of lowland systems.

RECOVERY

2.1 Trends at Galloway study sites

Monitoring of water chemistry, epilithic diatom assemblages and sediment trap diatom assemblages has continued at the Galloway study sites over the study period, and the resulting data stored in the CLAG chemistry-biology database. Harriman *et al.* (1995b) summarise trends in water chemistry and biology in the Galloway study lochs over the period 1978-94, and more recent trends in nitrate concentrations are summarised by Harriman (1988b).

2.2 Baseline data and trends at exceedance study sites

Repeat water chemistry and epilithic diatom samples have been taken from the exceedance study sites over the period of the programme. These data have been stored in the CLAG database.

2.3/2.4 Regional and national application of MAGIC-WAND

The MAGIC model has been calibrated to the sites in the UK Acid Waters Monitoring Network using a consistent methodology and best available data (Jenkins *et al.* 1997b) to assess the future response to the Second S Protocol and to assess the level of deposition required to induce surface water recovery at sites where the Second S Protocol is not predicted to promote a sustained recovery. In general, the model predicts only a small recovery in pH over the next 30 to 50 years. Beyond this, re-acidification is predicted to occur unless further reductions in S and/or N deposition are achieved. The benefit of targeting either S or N reductions is site specific and depends on the current deposition loads and the current and future N leakage from the catchment.

Techniques have been developed and tested to extrapolate the MAGIC model from headwater catchments to whole regions. These are based upon two different techniques; (i) multiple calibration methodology and (ii) monte-carlo procedures. These techniques have been tested in Galloway, Wales and for the whole UK (Evans *et al.* in press). The results point to a slow recovery in the Pennines, Galloway, Central Scotland and the Lake District and imply that greater emission reductions in N and S will be required to bring surface water ANC below 0 within 50 years in these areas. These deposition reductions may be achievable through N alone. National scale application of MAGIC7 is currently limited by inadequate soils chemistry data in England and Wales. An extensive soil sampling programme is now required to determine appropriate data to describe the C and N pools in catchment soils.

2.5/2.6 Chemistry-biology relationships

a) The CLAG chemical-biological database and analyses of species-chemistry relationships

An important aspect of the biological modelling work has been the development of a high quality chemical-biological database focused on diatoms and invertebrates

(Juggins 1998). The database has been assembled by merging existing datasets with new data collected during the current contract. The dataset contains records from 225 sites and are stored as a series of tables in a relational database managed using Microsoft Access97 software.

The database has been used to analyse species response to chemical variables as a first stage in assessing (1) which chemical variables are important in determining taxon distributions and so should be included in any predictive model, and (2) which taxa show a statistically significant relationship to streamwater pH.

Community ordination analysis indicates that a subset of chemical variables (pH, alkalinity, conductivity, Ca, Cl, SO₄ and total monomeric aluminium) effectively account for the dominant biological gradients in the diatom and invertebrate datasets. pH, total monomeric aluminium and conductivity, in that order, are the most important variables in accounting for the observed diatom and invertebrate distributions. 50 diatom taxa and 31 invertebrate taxa show statistically significant responses to pH. These results can be used to identify potential indicator taxa with varying degrees of tolerance to lowered pH. In addition, the fitted models also provide a quantitative description of taxon distribution that can potentially be used to predict the probability of occurrence, or relative abundance of each taxon at particular chemical values.

b) Invertebrate Biology

Prior to this phase of the DETR report, empirical models were developed that related stream invertebrate communities to combinations of mean pH, base cation concentration, aluminium and ANC (*MEDUSA: Models of Ecosystem Dynamics Under Stream Acidification*). These same models have been used to predict future biological response to altered deposition and altered stream chemistry. However, model tests involving liming indicated poor performance when the models had to predict biological effects by changing chemistry. Invertebrate response fell short of modelled expectations, and possible explanations were that; (i) model structure failed to account for other limits on distribution, such as stream habitat structure, or effects by food supply (ii) acid episodes, rather than mean chemistry, controlled invertebrate distribution; (iii) there were other dynamic limits to recovery, such as natural delays in invertebrates recolonizing streams that were recovering; (iv) other deteriorating aspects of stream chemistry, such as increasing nitrogen concentrations, might limit recovery; (v) background and stochastic variations in invertebrate communities might be too large for recovery to be detectable over short time-scales.

These points are being addressed at Lynn Brienne, and from further use of data from the Welsh Acid Waters Survey (WAWS). Hypotheses (i) and (ii) have been investigated during this phase of the work (Brewin *et al.* 1998). Further investigation of (ii) (iii) (iv) and (v) will occur in allied work, or during the next phase of this project.

Effects on invertebrates by habitat structure have been addressed using WAWS data in conjunction with the Environment Agency River Habitat Survey (RHS). These data show that correlations between invertebrate community composition, diversity and acid-base status subsume any correlation with habitat structure. For individual acid-

sensitive species, acid-base status and altitude only are highly significant predictors of distribution. The operation of *MEDUSA* is thus unlikely to be severely constrained by failing to account from habitat character. Nevertheless, as a result of this work, model algorithms and methods are now available that will allow *MEDUSA* to incorporate habitat effects.

There has been debate about whether invertebrates respond directly to food quality or directly to chemistry. Effects by food quality on acid sensitive invertebrates have thus been addressed using transplantation experiments. Since many are herbivores feeding by grazing and scraping stone surfaces, work has concentrated on one indicator species (the mayfly *Baetis rhodani*), and on its diatom food source. Transplantation of diatoms from acid streams (pH 4.5; mostly *Eunotia exigua*) into circumneutral streams (pH 7.2), and from circumneutral streams (mostly *Achnanthes minutissima var minutissima*) to acid, confirmed that diatom response to altered chemistry occurs within 4 weeks. Moreover, transplantation of *Baetis rhodani* into acid streams showed that death occurred even when food was provided from circumneutral streams. Similarly, nymphs survived in circumneutral streams even when provided with diatoms from acid streams. These results show that effects by water quality subsume those due to food quality. Impoverished food supplies are unlikely to be responsible for delayed invertebrate response to stream recovery

Effects by acid episodes on aquatic organisms have long been suspected, but seldom clearly demonstrated due to technical difficulties. Previous indications that invertebrate community composition reflected mean chemistry in part resulted from statistical artefacts, since mean values for pH or aluminium data also incorporated effects by episodic extremes. A method has now been developed through which baseflow chemistry is identified by examining modal values. Biological effects by episodic chemistry are then revealed by calculating variations during events relative to the modes for each stream. Using this approach, three stream types in Wales can be distinguished which are:

- circumneutral (modal pH 6.7; mean pH 6.6; minimum pH 6.1)
- episodically acid (modal pH 6.4; mean pH 6.0; minimum pH 5.0)
- chronically acid (modal pH 5.2; mean pH 5.4; minimum pH 4.5)

The same analysis shows that minimum pH, but not modal pH, explains most variation in invertebrate community composition and richness. Episodic effects will thus have to be built into *MEDUSA*,

Together, these results suggest that effects on invertebrates by acid episodes require further assessment. Dynamic elements will require incorporation into models of stream acidification, and possibly also into critical load sampling and modelling. The data also suggest that other limits on biological recovery, due to confounding effects by food supply or habitat structure, are less important. Other limits to recovery, such as recolonization, still prevent barriers to understanding.

2.7/2.8 Identification and biology of analogue sites

The fossil diatom based approach for identifying modern analogues for the pre-acidification conditions of acidified lakes has been further developed (Flower *et al.* 1997) and applied to acidified lakes in the Acid Water Monitoring Network (AWMN). These applications highlight relatively unpolluted sites in the north-west of Scotland (Allott *et al.* 1995c) as potential analogue lakes. Data on the biological characteristics of these lakes (e.g. diatoms and invertebrates) have been collected and are stored in the CLAG chemistry-biology database. These analogue lakes potentially provide restoration target ecosystems for the acidified lakes which can be used to evaluate the recovery process.

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