

## Chapter (not refereed)

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## **Introduction**

In June 1994 the United Kingdom government signed the European sulphur protocol which committed them to a 70% reduction in SO<sub>2</sub> emissions by the year 2005 and 80% by 2010, based on 1980 levels. This was the first instance of international legislation being formulated using the critical load concept. Notwithstanding the anticipated benefits to the environment of such reductions it was also recognised that such improvements could be diminished unless a similar approach was used to address the problem of increasing nitrogen emissions.

The Freshwater Sub-group of the UK Critical Loads Advisory Group (CLAG) has responsibility for evaluating available techniques for calculating critical loads for nitrogen and for establishing a scientific programme to address key issues and gaps in our knowledge of nitrogen dynamics. This paper summarises the preliminary findings of the Freshwater Group with respect to the nitrogen status and critical loads of UK freshwater.

## **General Considerations**

At its peak in the 1970's, the deposition of sulphur compounds accounted for about two thirds of the total acidic deposition in the UK. During the past 20 yrs this deposition has declined by up to 30% while emissions of oxidised nitrogen (NO<sub>x</sub>) have increased by nearly 20% as a result of emissions from motor vehicles. Ammonia emissions, especially from agricultural sources, have also increased significantly in recent years. When this situation and the projected future large (60-80%) reductions on S depositions are considered, it is clear that the relative importance of N deposition will increase dramatically.

Because the processes and pathways of nitrogen utilisation by vegetation, soils and water are far more complicated than for sulphur a more complex set of questions must be addressed, for example:

- a) Will different forms of N deposition (NO<sub>3</sub><sup>-</sup>; NH<sub>4</sub><sup>+</sup>) contribute equally and via similar processes to the acidification and eutrophication status of freshwaters?
- b) Can both acidification and eutrophication potential be quantified using similar models?
- c) How can seasonal variability in nitrate leaching be incorporated into critical load models?
- d) Is there a direct link between N inputs and surface water nitrate concentrations, and if so, how can the extent of N limitation be quantified?

Finally, bearing in mind the many complexities noted above, do we have acceptable methods to map critical loads and exceedance values for nitrogen (or total acidity).

### **Current Nitrogen Status of UK Freshwaters**

A preliminary evaluation of the current nitrogen status of UK Freshwaters has been made using the recently developed critical load database. This report will shortly be presented to the Department of Environment by the Freshwater Group. Although the relative contributions of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in precipitation are approximately equal in the UK, ammonium ions are rarely detected in surface water run-off in non-agricultural areas. Consequently only nitrate (and organic N) have been considered at the present time although this situation could change in the future.

The pattern of nitrate concentrations in UK surface waters (INDITE 1994) clearly reveals agricultural and urban influences in southern and eastern regions. However, by screening sites to include only those of high sensitivity ( $\text{Ca}^{++} < 300 \text{ eq l}^{-1}$ ), and excluding those with agricultural catchments, a clearer picture emerges which reveals two major features. Firstly, significant nitrate concentrations ( $>20 \text{ eq l}^{-1}$ ) occur in areas (eg Pennines and Cumbria) where S critical loads are already exceeded (See Harriman and Christie, 1993) and secondly, some sites (especially in central and north west Scotland) exhibit negligible nitrate leaching even though N inputs are quite large. To quantify the relationship between leaching and deposition a matrix was derived for all 584 UK sites which fitted the above sensitivity/land-use criteria (Table 1). While the general trend is for greater nitrate leaching at higher N inputs about 50% of these sites still retain most of the deposited N in the terrestrial ecosystem, even at some sites where N deposition exceeds  $1.0 \text{ K eq ha}^{-1} \text{ yr}^{-1}$ .

A preliminary assessment of the factors which determine the seasonal pattern of nitrate levels was made using monthly data from sensitive, high-elevation lochs in Galloway, south west Scotland, where vegetation, soil type and N inputs were as similar as possible. Even under these circumstances significant differences were found in the pattern of nitrate leaching at these sites (Fig. 1), suggesting that each was at a different stage of nitrogen saturation. Stoddard (1994) suggested a four stage saturation classification (0-3) ranging from stage 0 when concentrations remained low all year, with little or no seasonality, to stage 3 when concentrations remained high all year, again with little or no seasonal change. The Galloway lochs appear to exhibit all the stages of saturation apart from stage 3 as shown by the distinct groups of lochs in Figure 1. Superficially the main differences between these systems appear to be soil depth, lake depth, flushing rate and lake to catchment area which suggests that hydrological and physical properties of systems may also be important.

### **Calculating Critical Load and Exceedance Values for Nitrogen**

The following models are being used by the Freshwater Group to determine critical load and exceedance values for UK freshwater. Some preliminary maps are presented but at this early stage many caveats must be applied.

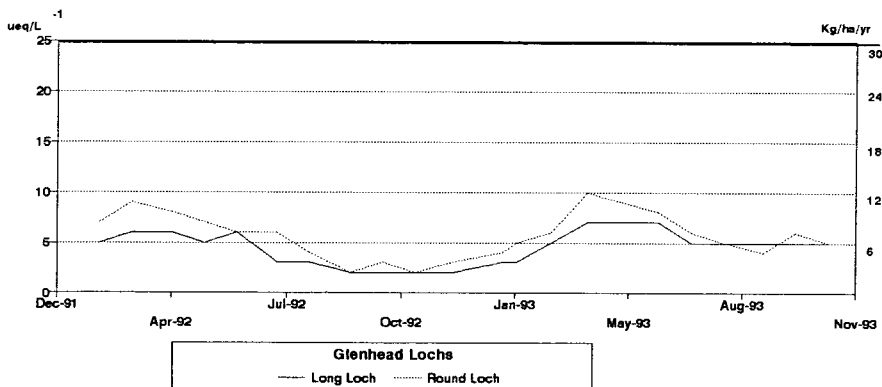
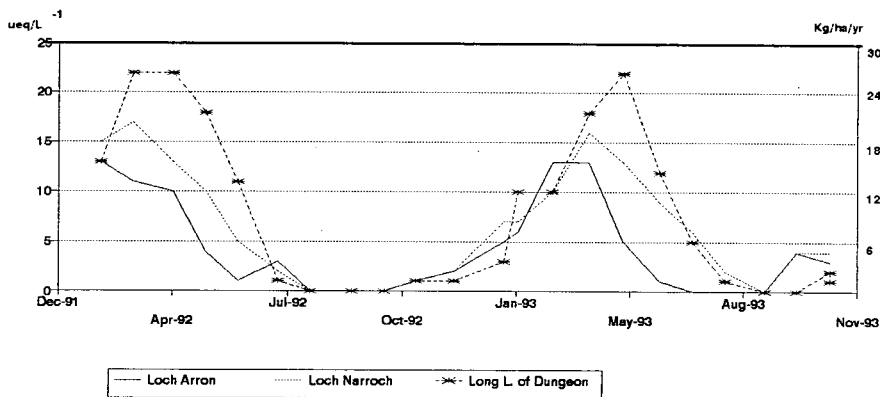
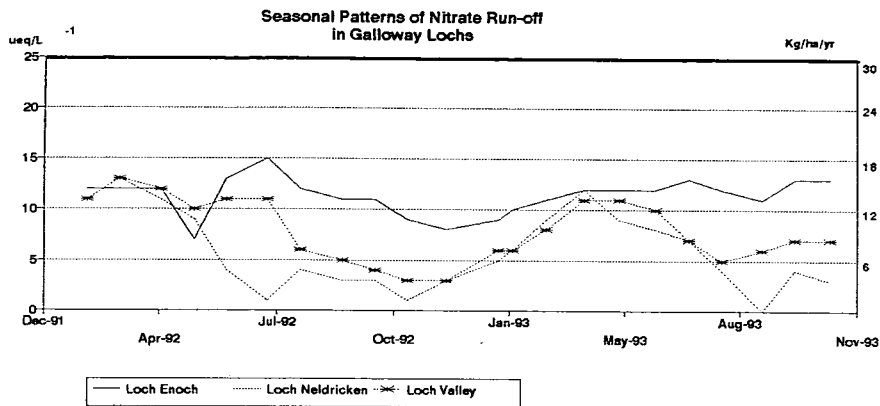


Figure 1 Seasonal patterns of nitrate run-off in Galloway lochs, south-west Scotland.

## Steady-state Water Chemistry model (SSWC)

This method was developed by Kämäri *et al.* (1992) and uses the same methodology as that applied to sulphur

$$\text{i.e.} \quad \text{CL}_{AC} = Q ([\text{BC}^*]_0 - [\text{ANC}]_{\text{limit}}) - \text{BC}^*_{\text{dep}} \quad (1)$$

This only differs from the sulphur value in that a lower  $\text{BC}_0$  concentration is obtained to account for the extra base cation losses due to N leaching. The critical load values derived from equation (1) are effectively the true total acidity loading as they reflect both N and S leaching. One important advantage of this method is that N input data are not required to calculate exceedance values because nitrate leaching is assumed to equal N sources minus N sinks.

$$\text{i.e.} \quad N_{\text{leach}} = N_{\text{dep}} - N_S \quad (2)$$

where  $N_S$  represents all sinks of N in the catchment.

The formulation in equation 2 represents a generalised situation where current N leaching is a consequence of long-term N deposition. Nevertheless it should be appreciated that current N leaching can change significantly in the short-term, independent of N deposition. This situation is usually caused by changes in the N dynamics of soils and vegetation, especially in managed catchments.

Consequently exceedance of the critical load of total acidity can be derived from

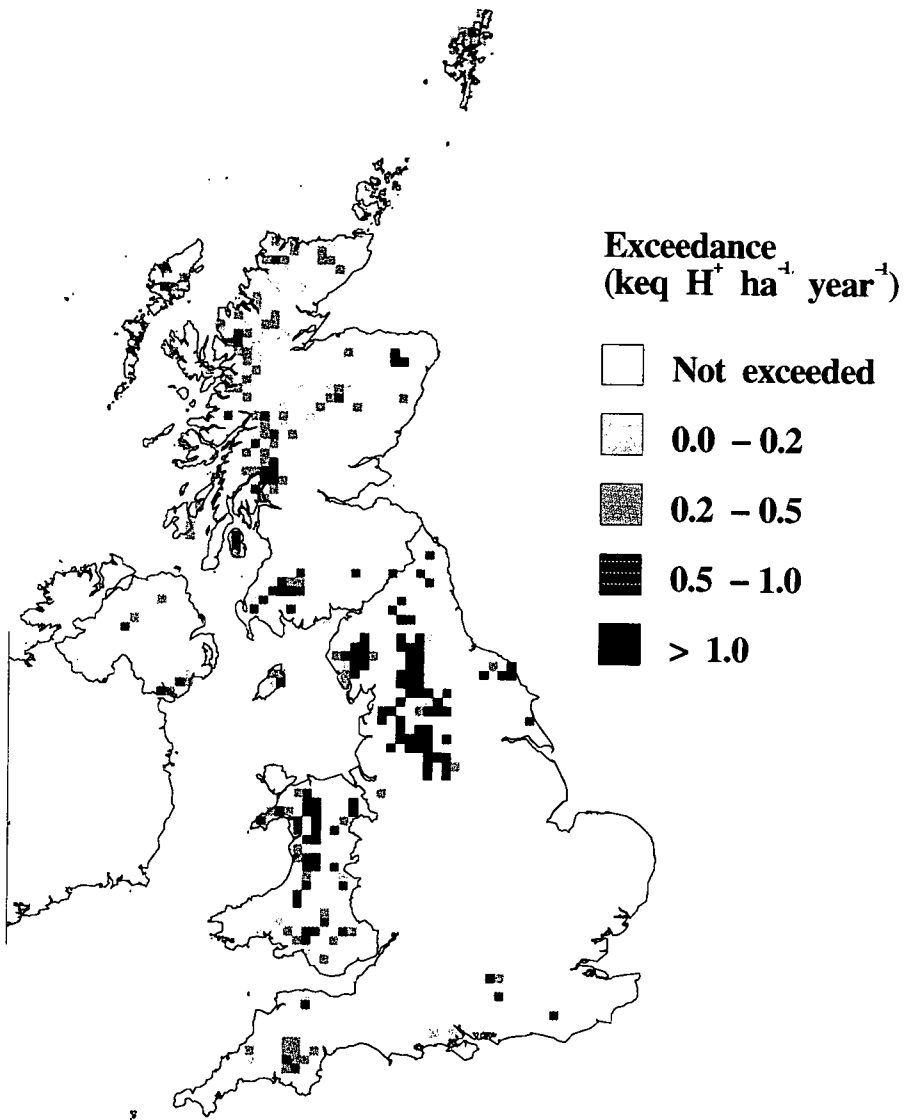
$$\text{Ex}_{AC} = S_{\text{dep}} - N_{\text{leach}} - \text{BC}^*_{\text{dep}} - \text{CL}_{AC} \quad (3)$$

No individual critical loads of N and S can be assigned by this method.

Provisional exceedance maps produced by this model for UK fresh waters (Fig. 2) are similar to those for sulphur indicating that N impacted sites are generally in the same areas of the UK as those affected by S inputs (i.e. Upland Wales, Pennines, Lake District and south west Scotland). Therefore, although the distribution of exceeded squares remains relatively unchanged the number of sites in the high exceedance band ( $> 1.0 \text{ Keqha}^{-1}\text{yr}^{-1}$ ) increases.

## Diatom Critical Loads Model (DCL)

The DCL model is complementary to the SSWC model and is based on the general observation that diatom flora retained in sediment profiles show little or no change in species composition prior to the onset of anthropogenic acidification. Any shift to a more acidophilous diatom flora can be considered as a "point of change" which is analagous to exceedance of the critical load for that specific and usually very sensitive biological indicator. Development of the methodology for calculating critical loads is described by Battarbee *et al.* (1993) but essentially the model uses relationships between pre-acidification calcium concentrations in water (as a measure of site sensitivity) and present day sulphur and nitrogen loadings. This relationship was derived from 41 UK lakes which gave accurate diatom records and calibrated using logistic regression to calculate the probability of acidification for different calcium to loading ratios. At the optimum discrimination, giving a probability of acidification of 50%, a ratio of 94:1 was found. The model is currently being adapted to provide critical loads, and critical load exceedances, for total acidity (sulphur and nitrogen). Exceedance values for total acidity require a measure of the fraction of deposited nitrogen leached into the surface waters. This is calculated from



**Figure 2:** Exceedance of critical loads for total acidity for UK freshwaters (revised SSWC model)

the differences between the proportions of sulphate/nitrate in the water and sulphur/nitrogen deposition modelled for the site. In this way the fraction of the nitrogen deposition contributing to acidification can be added to the value of sulphur deposition to provide total "effective" acid deposition. The critical ratio used in the diatom model has also been recalibrated using total effective deposition rather than sulphur deposition, giving a ratio of 89:1. Critical loads for total acidity are calculated using this ratio.

A preliminary map of UK critical load exceedances for total acidity has been prepared using the diatom model (Fig. 3). Superficially this mirrors the exceedance map for sulphur deposition alone as the areas most severely impacted by nitrogen deposition are also those with high exceedances for sulphur. However, calculations of the increase in exceedance due to the inclusion of leached nitrogen deposition demonstrate that for large parts of the UK (e.g. Cumbria, the Pennines, Galloway) nitrogen deposition by itself could account for significant exceedances. This finding has implications not only for the regional extent of acidification, but also for the extent of recovery at these sites if only sulphur deposition is reduced.

### First Order Acidity Balance (FAB) Model

The SSWC and DCL models only provide information on present day exceedances of critical loads. For estimates of potential future exceedances the FAB model should be used. This model is based on an acidity mass balance and includes rate-limited processes for denitrification and in-lake retention which are assumed to increase with increasing N inputs.

The full charge balance for a lake and its catchment can be described as follows:

$$N_{dep} + S_{dep} = fN_u + (1-r)(N_i + N_{de}) + rN_{ret} + rS_{ret} + BC_l - ANC_l \quad (3)$$

where

$N_{dep}$  = deposition of N

$S_{dep}$  = deposition of S

$N_u$  = net growth uptake of N by vegetation

$N_i$  = immobilisation of N in the catchment soils

$N_{de}$  = N denitrified in the catchment soils

$N_{ret}$  = in-lake retention of N

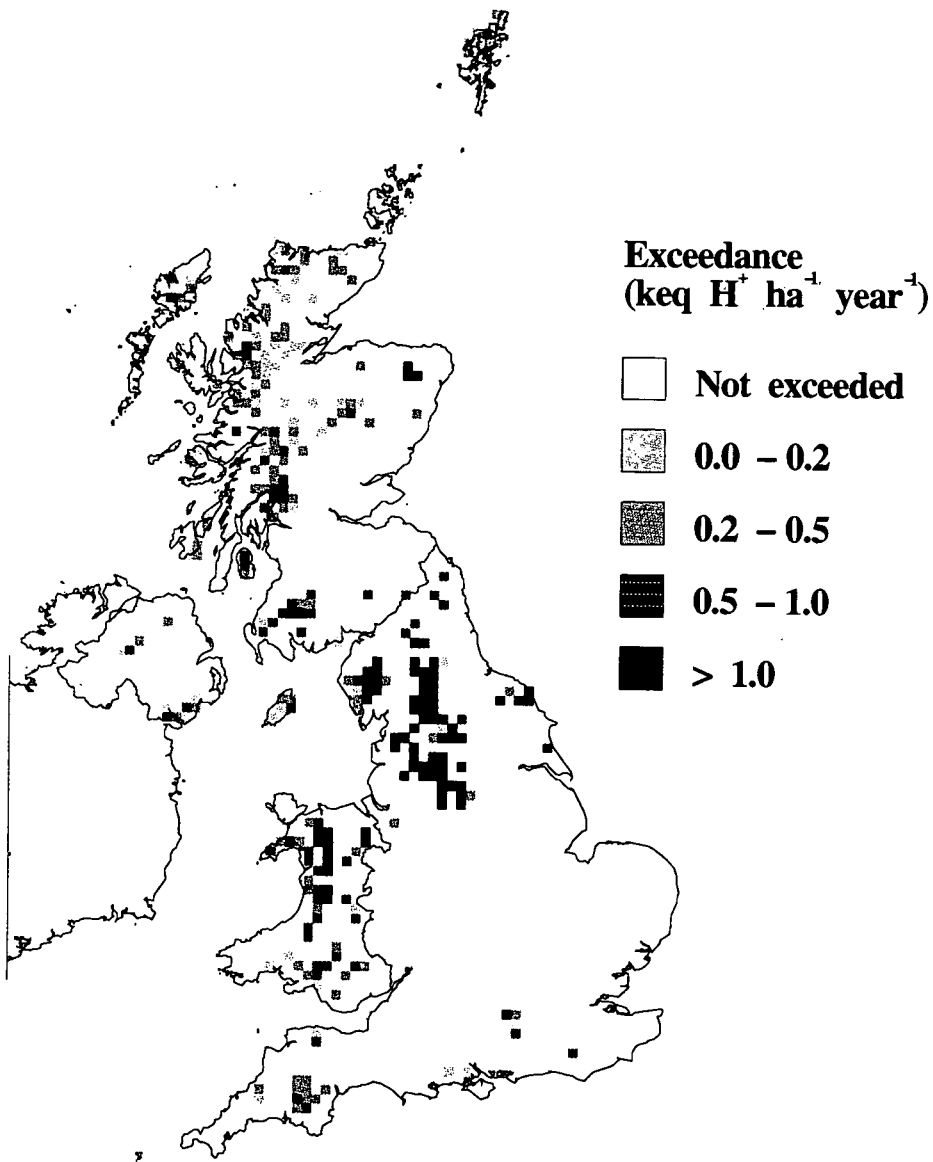
$S_{ret}$  = in-lake retention of S

$BC_l$  = base cations leaching from the catchment

$ANC_l$  = ANC leaching from the catchment

$f$  = fraction of forested area in the catchment

$r$  = lake: catchment area ratio



**Figure 3:** Exceedance of critical loads for total acidity for UK freshwaters (revised diatom model).

Full details of the development of this model are given by Kämäri *et al.* (1992) and Posch *et al.* (1993) and further modifications are described by Henriksen *et al.* (1993). The key derivations for mapping requirements are discussed below. By incorporating relationships for denitrification and in-lake reten-



tion equation (3) can be modified to give:

$$a_N N_{dep} + a_S S_{dep} = b_1 N_u + b_2 N_i + Q([BC^*]_0 - [ANC]) \quad (4)$$

where the dimensionless constants  $a_N$ ,  $a_S$ ,  $b_1$  and  $b_2$  are all smaller than one and depend on lake and catchment properties alone:

$$a_N = (1 - f_{de})(1 - \rho_N)$$

$$a_S = 1 - \rho_S$$

$$b_1 = f(1 - f_{de})(1 - \rho_N)$$

$$b_2 = (1 - \tau)(1 - f_{de})(1 - \rho_N)$$

By choosing an appropriate ANC limit, equation (4) then converts to the critical load expression:

$$a_N CL(N) + a_S CL(S) = b_1 N_u + b_2 N_i + Q([BC^*]_0 - [ANC]_{limit}) \quad (5)$$

Exceedance of critical load can now be calculated by subtracting the right side of equation (5) from the left side of equation (4)

$$Ex(N_{dep}, S_{dep}) = a_N N_{dep} + a_S S_{dep} - b_1 N_u - b_2 N_i - L_{crit} \quad (6)$$

where

$$L_{crit} = Q([BC^*]_0 - [ANC]_{limit})$$

which is the same formulation as the SSWC model.

If the potential nitrate leaching is required (for example, to compare with current N leaching or to insert in the SSWC model to calculate future exceedances) this can be calculated by subtracting sources and sinks of N.

i.e.

$$N_i = a_N N_{dep} - b_1 N_u - b_2 N_i \quad (7)$$

Alternatively the critical load for nutrient nitrogen can be calculated by fixing  $N_i$  at a value which for any system, would not cause eutrophication.

$$CL_{nut}(N) = (b_1 N_u + b_2 N_i + N_{i,crit}) / a_N \quad (8)$$

Because of the substantial data requirements for different catchment types no provisional maps have yet been produced using this model. A full description of the updated version of the FAB model is given in Posch.

A few general points should be emphasised when comparing the output from these models.

1. The potential nitrate leaching derived from the FAB model may not be directly transferable to the SSWC model because the former model relates to leaching below the rooting zone while the latter (SSWC model) uses nitrate values for water which has travelled through all soil and geological pathways.
2. The minimum critical load of nitrogen  $CL_{\min}(N)$  represents the point where nitrate will begin to leach into freshwater (i.e. by setting  $N_{l,crit}$  at zero in equation (8)). Conversely the maximum critical load for nitrogen  $CL_{\max}(N)$  equates to  $CL_{\min}N + L_{crit}$ .
3. The key input parameter in the SSWC model is nitrate leaching, therefore to account for seasonality some estimate of a flow weighted mean value should be used.
4. In the FAB model the key parameters are  $N_u$  (nitrogen growth uptake by vegetation) and even more importantly,  $N_i$  (nitrogen immobilisation in soils).

Accurate estimates of these parameters are urgently required for upland UK catchments of different soil and vegetation type.

## Level II Analysis (Dynamic Models)

The requirements for a dynamic modeling approach to nitrogen is perhaps even more urgent than for sulphur because of the complexity of nitrogen dynamics in the terrestrial ecosystem. Predicting long-term changes requires a model which incorporates most of the key time-dependent variables. For sulphur the Freshwater Group used the MAGIC model to assess the impacts of different deposition scenarios while for nitrogen a derivative of MAGIC has been developed.

MAGIC-WAND (MAGIC-With Aggregated Nitrogen Dynamics) builds directly on MAGIC and allows the main fluxes and transformations of nitrogen to be independently specified at each time-step. MAGIC-WAND has been specifically developed for wide application and scenario assessment. It maintains the sulphur based chemistry dynamics of MAGIC and considers reduced and oxidised nitrogen species. The model requires specification of nitrification, mineralisation, fixation and denitrification rates and changes in these fluxes through time. Plant uptake is non-linear and dependent upon external nitrogen concentrations. A wide range of data describing these rates and fluxes have been reported and are reviewed to aid in model calibration.

The main sensitivity of the model lies in the selection of the parameters which describe the hyperbolic uptake function. Literature data can provide ranges for these values but specific catchment related values are not obtainable since the model is conceptual. Selection of uptake parameters must reflect catchment vegetation and vegetation change through time. Further observational and experimental work to determine nitrogen fluxes and dynamics at different ecosystems is required to facilitate site specific and regional model applications. It is already clear that the data requirements for validation of nitrogen models is extensive and will require detailed knowledge of the nitrogen status of UK catchments.

Details of recent developments in nitrogen models and their use in calculating critical loads for nitrogen are reported by Ferrier *et al.* (1995) in this volume.

## Conclusions and Recommendations

If the mass balance approach is the preferred method for mapping critical loads and exceedances for the major ecosystem components, then the following studies are recommended, bearing in mind that many upland catchments are leaking nitrate and may have already reached a critical saturation stage.

Priorities are:

1. To establish a programme of intensive nitrogen monitoring at a range of UK sites (e.g. Galloway, Pennines, North Wales, SW Scotland and N Scotland) to assess spatial and temporal variability in relation to N deposition and catchment characteristics so that appropriate N leaching values can be obtained.
2. To determine the key catchment conditions that lead to N leaching by establishing a range of key reference sites where simultaneous measurements of water, soils, vegetation and N deposition can be made. This information is vital for the development of dynamic models that simulate N behaviour in catchments.
3. To assess the impact of elevated N concentrations on the biology of upland waters with regard to acidification, eutrophication and species composition changes. Information on the extent of N limitation (as opposed to P) in upland waters is essential and this may require N manipulation experiments to speed up the interpretation of biological impacts.
4. Because many upland sites appear to be extremely sensitive and exceeded by nitrogen alone it may be appropriate to make more extensive use of freshwater maps for N protocols.

## Acknowledgements

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## References

- Battarbee, R.W., Allott, T.E.H., Kreiser, A.M. and Juggins, S. (1993)** Setting critical loads for UK surface waters: the diatom model. In: *Critical loads: concept and applications*. Eds: M. Hornung and R.A. Skeffington, 99-102. ITE symposium 28 HMSO, London.
- Ferrier, R.C., de Vries, W. and Warfvinge, P. (1995)** The use of dynamic models for the determination of critical loads for nitrogen - developments since Lökeberg. (This volume).
- Harriman, R. and Christie, A.E.G. (1993)** Evaluation of the steady-state water chemistry method for surface waters. In: *Critical loads: concept and applications*. Eds: M. Hornung and R.A. Skeffington 103-108 ITE Symposium 28 HMSO, London.
- Henriksen, A. Forsius, M. Kämäri, J., Posch, M. and Wilander, A. (1993)** Exceedance of critical loads for lakes in Finland, Norway and Sweden: reduction requirements for nitrogen and sulphur deposition. Report 32/1993 NIVA report for Nordic Council of ministers. 46pp.

- Kämäri, J., Jeffries, D.S., Hessen, D.O., Henriksen, M., Posch, M. and Forsius, M. (1992)**  
Nitrogen critical loads and their exceedance for surface waters In: Grennfelt, P. and Thörmelöf, E. (Eds). Critical loads for nitrogen Nord 1992-41 Nordic Council of Ministers, Copenhagen, Denmark pp161-200.
- Posch, M., Forsius, M. and Kämäri, J. (1993)** Critical loads of sulphur and nitrogen for lakes. I: Model description and estimation of uncertainty. Water, Air and Soil Pollution 66. pp173-192.