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Critical loads of sulphur and nitrogen for freshwaters in Great Britain and assessment of deposition reduction requirements with the First-order Acidity Balance (FAB) model

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Key Words: critical loads, acidification, nitrate, FAB model, acid deposition

Abstract

The critical loads approach is widely used within Europe to assess the impacts of acid deposition on terrestrial and freshwater ecosystems. Recent work in Great Britain has focused on the national application of the First-order Acidity Balance (FAB) model in order to take account of the acidifying effects of nitrogen (N) as well as sulphur (S) deposition on sensitive lakes and streams. The FAB model is applied to a freshwaters dataset of 1470 lake and stream water chemistry samples from sites across Britain which were selected to represent the most sensitive water bodies in their corresponding 10 km grid square. A "Critical Load Function" generated for each site is compared with the current deposition load of S and N at the time of water chemistry sampling. 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 μeql^{-1} at more than a quarter of the sites sampled, i.e. the critical load of acid deposition is exceeded at these sites. The critical load exceedances are generally found in upland regions of high deposition where acidification has been previously recognised, but critical loads in large areas of western Scotland are also exceeded where little biological evidence of acidification has yet been found. There is a regional variation in the deposition reduction requirements for protection of the sampled sites. The FAB model indicates 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. Current international commitments to reduce S deposition throughout Europe will therefore be insufficient to protect the most sensitive freshwaters in England and Wales.

Introduction

Acid deposition, in the past originating mainly from the oxidized sulphur compounds released by fossil fuel combustion, has long been recognised as an environmental problem on an international scale. The acidification of soils and waters, and subsequent damage to sensitive ecosystems, has been linked to atmospheric pollution in wide-ranging studies spanning many countries. As a result, international strategies have been negotiated for the control and abatement of sulphur emissions, culminating in the Second Sulphur Protocol under the Convention on Long Range Transboundary Air Pollution, signed in Oslo in 1994 (UNECE, 1994).

The Oslo Protocol was underpinned scientifically by critical loads models linking sulphur deposition fluxes to selected measures of environmental damage (Bull, 1995). These models were used to produce national and international maps of both critical loads, indicating the most acid sensitive areas, and critical load exceedances, showing the regions where acidification impacts on specified receptors were greatest (e.g. Kämäri *et al.*, 1992, 1993, Henriksen *et al.*, 1992, Langan and Wilson, 1994, Sverdrup *et al.*, 1994, CLAG, 1994). The maps introduced an "effects-based" method for spatial targeting of emission abatement measures, thereby providing a useful policy tool.

For freshwaters, the Steady-State Water Chemistry (SSWC) model was used to generate critical load and exceedance maps of sulphur for Scandinavia and the UK (Henriksen *et al.*, 1992, CLAG Freshwaters, 1995). The SSWC model was employed because of its modest data requirements, needing only water chemistry data in order to calculate the critical load, and an estimate of sulphur deposition in order to determine whether the critical load was exceeded. The key to the simplicity of the model is the assumption that the sulphate anion is mobile in catchments (Seip, 1980, Henriksen, 1984), so that input fluxes of sulphate as acid deposition will equal output fluxes of sulphate in the runoff from a catchment. Empirical relationships are employed to derive the original, pre-industrial leaching rate of base cations from a lake or stream catchment using only measured water chemistry. If a critical acid neutralizing capacity (ANC) concentration is selected from known relationships with biological response, it can be converted into a critical flux in catchment runoff and used to derive the long-term critical load (Henriksen *et al.*, 1992).

The Oslo Protocol ensured that measures would be adopted for the abatement of sulphur emissions across Europe, but current diplomatic efforts are directed towards the negotiation of a similar protocol for nitrogen. It has been recognised in recent years that with a decline in sulphur deposition, the role of nitrogen in acidification will increase in relative and perhaps absolute terms, and many recent studies have noted the significance of nitrate in acid sensitive waters (Stoddard, 1994, Allott *et al.*, 1995, Dise and Wright, 1995, Henriksen *et al.*, 1997). The protons associated with both nitrate and ammonium ions (in the latter case via nitrification) in acid deposition will contribute to the acidification of surface waters in exactly the same way as sulphate-based acidity, with an equivalent reduction in acid neutralizing capacity (ANC).

While the assumed mobility of the sulphate anion in catchments enables the conversion of deposition fluxes into surface water runoff fluxes, the same assumption cannot be made for nitrogen (N). The complex biological interactions affecting the transport of N (and hence its associated H^+) through catchments, and the presence of mechanisms for the removal or long-term storage of N in catchment soils and vegetation, mean that it is not possible to use a single set of empirical relationships to link deposition and surface water chemistry. Instead, a process-oriented model is required which can be used to quantify the proportion of total N deposition which is transported through the terrestrial part of a catchment into the surface waters.

One such model which has been used for the derivation of linked critical loads for nitrogen (N) and sulphur (S) is the First-order Acidity Balance (FAB) model (Posch *et* *al.*, 1997, UBA, 1996, Henriksen, 1998). The FAB model employs a simple charge balance for N and S, along with the original base cation leaching rate from the SSWC model, in order to construct a "critical load function" (CLF) which quantifies the deposition reduction requirements for either N or S, given the value of the other.

The FAB model is here applied to British freshwaters to evaluate the long term impacts of current levels of acid deposition, and to assess the requirement for reductions in both sulphur and nitrogen deposition in order to protect the most sensitive freshwater ecosystems across the country.

2. Modelling methods and data requirements

2.1 Model description: critical loads

The application of the SSWC model to UK freshwaters has been described in reports by the Critical Loads Advisory Group (CLAG) to the UK government (CLAG, 1994, CLAG Freshwaters, 1995). The SSWC model has to be employed in the first instance in order to provide the pre-industrial base cation leaching, which is in turn required for the definition of critical acid anion flux and hence critical load.

Freshwater critical loads are based upon the maintenance of ANC above a critical concentration with respect to a specific target organism, so it is first necessary to consider their definition. ANC can be calculated indirectly as a charge balance (Henriksen *et al.*, 1992):

$$[ANC] = [BC]^* - [AN]^* = [HCO_3^-] + [A^-] - [H^+] - [Al^{n+}] \qquad \textit{(Equation 1)}$$

where $[BC]^* = \Sigma$ non-marine base cations
$[AN]^* = \Sigma$ non-marine acid anions
$[HCO_3^-]$ = bicarbonate ion
$[A^-]$ = organic anions
$[H^+]$ = hydrogen ion
$[Al^{n+}] = \Sigma$ positively charged Al species

i.e.

$$[ANC] = [Ca^{2+}]^* + [Mg^{2+}]^* + [Na^+]^* + [K^+]^* - [SO_4^{2-}]^* - [NO_3^-] \qquad \textit{(Equation 2)}$$

Note that the superscript "*" signifies the non-marine component, calculated using chloride as a tracer from the constant ionic composition of seawater. It is assumed that all measured chloride is of marine origin and therefore delivered with an equivalent amount of base cations (although HCl deposition may be locally significant close to power stations). The marine component of atmospheric inputs is neutral and so is assumed to have no net effect on ANC.

Since ANC is defined as the sum of base cations minus the sum of strong acid anions (Henriksen *et al.*, 1992), the critical flux of acid anions (i.e. critical sulphur deposition) is simply the difference between sustainable base cation leaching and the critical ANC flux. While the availability of exchangeable base cations in the soil complex may offer short-term buffering against acidification, in the long term steady-state considered by critical load models (decades and longer, e.g. Posch *et al.*, 1997, Jenkins *et al.*, 1997), only the supply of base cations from weathering provides a permanent buffer (i.e. is not a transient response), and it is this value, minus the required level of ANC protection, which determines the critical load (Posch *et al.*, 1997).

The basis of the SSWC model is to calculate the flux of acid anions which, when combined with the long-term flux of base cations from weathering, will maintain ANC concentrations above the critical value:

$$L_{crit} = Q\,([BC]_0^* - ANC_{crit}) \qquad \textit{(Equation 3)}$$

where L_{crit} is the critical leaching flux of acid anions, Q is catchment runoff, $[BC]_0^*$ is the pre-industrial concentration of non-marine base cations and ANC_{crit} is the pre-selected critical ANC threshold.

ANC_{crit} can be selected according to the required protection level for a given target organism, and the choice is therefore an arbitrary, political one. For freshwater critical loads modelling within Europe, the chosen target organism is usually brown trout (*Salmo trutta*), a fish of widespread distribution and economic importance in many upland areas of Europe. The correlation between the health of brown trout populations and ANC has been demonstrated through extensive studies in Scandinavia, and response curves have been derived to link the percentage of lakes holding healthy, reduced or extinct brown trout populations with ANC (Lein *et al.*, 1992). The requirement for an ANC value of 20 μeql^{-1} or 50 μeql^{-1}, as adopted in Scandinavian countries (Henriksen *et al.*, 1992), was deemed too stringent for British lakes where naturally occurring ANC values close to zero were found (CLAG, 1994): such ANC values could only be achieved by liming in some areas of Britain, even with zero acid deposition. For Britain a critical ANC value of 0 μeql^{-1} is therefore employed, which corresponds with a fifty percent probability of damage to brown trout populations (Lein *et al.*, 1992).

In the formulation of the SSWC model for sulphur (Henriksen *et al.*, 1992), L_{crit} is equivalent to the critical load for sulphur, because all deposited sulphur will at steady-state be present (it is assumed) in the runoff: the critical deposition flux is equal to the critical leaching flux of sulphate. In contrast, the FAB model employs a charge balance of acid anions to define those combinations of S and N deposition which will result in the critical leaching flux of acid anions (sulphate plus nitrate) over the longer term (decades).

Since ANC_{crit} is pre-selected, the unknown quantity is $[BC]_0^*$, which is estimated from the relationship between base cation leaching and the deposition inputs of strong acid anions, according to the so-called "F-factor" (Brakke *et al.*, 1990):

$$[BC]_t^* - [BC]_0^* = F\,([AN]_t^* - [AN]_0^*)$$

or $[BC]_0^* = [BC]_t^* - F([AN]_t^* - [AN]_0^*)$ *(Equation 4)*

where the subscript "t" indicates a current concentration and the subscript "0" indicates the pre-industrial concentration. $[SO_4^{2-}]_0^*$ is estimated from an empirical relationship with $[BC]_t^*$ derived for near-pristine lakes in northern Norway (Henriksen *et al.*, 1990). Pre-industrial nitrate concentrations are assumed to have been zero, which is supported by current observations in lakes in northern Scotland where current N deposition levels are among the lowest in the country (RGAR, 1997). The change in base cation leaching per unit change in acid anion leaching is F, calculated according to the methodology of Brakke *et al.* (1990):

$$F = \sin\left(\frac{\Pi}{2}\frac{[BC]_t^*}{S}\right) \qquad \textit{(Equation 5)}$$

where *S* is a constant which varies regionally according to geology, but from empirical studies is taken as 400 μeql^{-1} (Harriman and Christie, 1995). This means that in a surface water with $[BC]_t^* = 400$ μeql^{-1}, the high base cation concentration indicates a weatherable catchment mineralogy likely to ensure the complete neutralization of incoming acidity, i.e. it is assumed that F=1. Where measured base cations exceed the concentration *S*, F has to be set to 1, otherwise it would decrease again according to the sine function.

It is now possible to calculate $[BC]_0^*$ and hence L_{crit}, which becomes an input parameter to the FAB model. A charge balance incorporating the major processes affecting the acid anion budget is then invoked (Posch *et al.*, 1997):

(Equation 6)

$$\underset{\textit{atmospheric inputs}}{\mathbf{N_{dep} + S_{dep}}} = \underset{\textit{"internal" catchment processes}}{\{f\mathbf{N_{upt}} + (1-r)(\mathbf{N_{imm}} + \mathbf{N_{den}}) + r(\mathbf{N_{ret}} + \mathbf{S_{ret}})\}} + \underset{\textit{leaching export}}{\mathbf{AN_{leach}}}$$

N_{dep} = total N deposition
S_{dep} = total S deposition
N_{upt} = net growth uptake of N by forest vegetation (removed by harvesting)
N_{imm} = long term immobilisation of N in catchment soils
N_{den} = N lost through denitrification in catchment soils
N_{ret} = in-lake retention of N
S_{ret} = in-lake retention of S
AN_{leach} = acid anion leaching from catchment
f = fraction of forested area in the catchment
r = lake:catchment area ratio

All units are expressed in equivalents (moles of charge) per unit area and time. Braces enclose "internal" catchment processes, i.e. those terrestrial and in-lake processes which operate on acid anion inputs to control the net export in catchment runoff.

The charge balance equates the deposition inputs of acid anions with the sum of processes which control their long term storage, removal and leaching exports. Several major assumptions are made in this formulation:

1. long term sinks of sulphur in the terrestrial part of the catchment (soils and vegetation) are negligible,
2. there are no significant N inputs from sources other than atmospheric deposition, i.e. no fertiliser application in the catchment,
3. ammonium leaching is negligible because any inputs are either taken up by the biota, adsorbed onto soils, or nitrified to nitrate.

The internal catchment processes affecting acid anion budgets introduced by the FAB model are linked to vegetation cover, soil type and catchment morphology. For modelling applications in Britain, the calculation of these sink terms is described by Curtis *et al.* (1998a).

Net growth uptake of N (in forest)

Over the long timescales (10^1-10^2 years) considered by critical loads modelling, the only permanent sinks for N in the biomass occur when there is some form of harvesting or removal of biomass from the catchment. Short term, seasonal cycling of N does not affect the mean annual budget over this timescale. The main route for the removal of biomass from upland catchments is therefore through the harvesting of forest. There are estimates available for the N content of various tree species, and if the time period of the harvesting cycle is known, a long-term figure for the export of nitrogen can be derived. For example, Emmett and Reynolds (1996) estimate the potential removal of nitrogen in thinnings and bolewood during harvesting of Sitka spruce stands of Yield Class 6 to 24 to be in the range 1.0-8.5 kgN ha^{-1} yr^{-1} for the UK. These figures assume harvesting at 40 years of age. It is recognised that the annual uptake of nitrogen will not be constant throughout the 40 years of forest growth, because there is a link between N uptake and tree age (Emmett *et al.*, 1993, Reynolds *et al.*, 1994).

Ideally, forestry data (species, age, yield class) should be used to determine N removal rates on a local basis. For national mapping, these data are not available so a default value in the mid-range of the published data (Emmett and Reynolds, 1996) is employed here (N_{upt} = 0.279 keq ha^{-1} yr^{-1} or c. 4 kgN ha^{-1} yr^{-1}) for catchments containing areas of coniferous forest.

Other possible routes for N export in biomass include grazing (weight gain of livestock) and burning (e.g. of heather on grouse moors) but these are assumed here to be negligible in the acid sensitive upland catchments of Britain.

Long term immobilisation of N in catchment soils

Estimates of the long term immobilisation of N in catchment soils have been derived by chronosequence studies, whereby the total N content of soil profiles is divided by the age of the profile (often assumed to be approximately 10,000 years since the last glaciation) to determine the annual immobilisation rate (UBA, 1996). These long-term estimates suggest a low immobilisation rate in the range 0.5-1.0 kgN ha^{-1} yr^{-1}. Under present conditions with high growth due to elevated N deposition this range may extend to a much higher figure, and shorter term studies of the recent increases in N content in soil profiles indicate values of up to 10 kgN ha^{-1} yr^{-1} (UBA, 1996). For

British soils, the working range adopted by the CLAG soils subgroup is 1-3 kgN ha^{-1} yr^{-1}, depending on soil type (Hall *et al.*, 1997).

Denitrification

It is assumed that N immobilisation and growth uptake are faster processes than denitrification (Posch *et al.*, 1997), and that denitrification can be linearly related to the net input of nitrogen into the soil system as follows:

$$N_{den} = f_{de}\,(N_{dep} - N_{imm} - fN_{upt}) \qquad \textit{(Equation 7)}$$

where f_{de} is the "denitrification fraction", with a value between 0 and 1, ascribed to the catchment soils.

Posch *et al.* (1997) have argued that peat soils are likely to provide the highest rates of denitrification, and proposed a method for the calculation of a "denitrification fraction". Denitrification is an anaerobic process and therefore a function of soil moisture content, which is very high in most peat soils. They assumed that in peat soils, denitrification of net nitrogen inputs could be 80%, while the minimum denitrification fraction for other soil types would be around 10%. The denitrification rate for a catchment can therefore be estimated by an interpolation of these figures:

$$f_{de} = 0.1 + 0.7 f_{peat} \qquad \textit{(Equation 8)}$$

where f_{de} is the denitrification fraction, and f_{peat} is the proportion of peat soils within the catchment. Denitrification within any catchment therefore varies between 10% and 80% of net inputs. This approach has been used in several countries around Europe, as recommended by the UNECE (UBA, 1996).

The problem with the above method for determining denitrification is that the resulting denitrification rate may be far higher than current values measured for British soils. For example, for peat soils $f_{de} = 0.8$, which implies that 80% of net N inputs (after N uptake and N immobilisation) are denitrified. With total N deposition exceeding 30 kgN ha^{-1} yr^{-1} across some parts of upland Britain (RGAR, 1997), the denitrification rates for unafforested peat catchments, after subtracting the component immobilised in catchment soils (a figure of 1-3 kgN ha^{-1} yr^{-1} is used for Britain), equate to 80% of at least 27 kgN ha^{-1} yr^{-1}, i.e. more than 21 kgN ha^{-1} yr^{-1}. This value is an order of magnitude higher than observed denitrification values for peat soils in Britain (Emmett and Reynolds, 1996) and five times greater than the recommended maximum value for UK soils (Hall *et al.*, 1997).

For the British application of the FAB model the denitrification rate is given a fixed value for certain soil types, independent of deposition. Each of the soil map units on the 1:250,000 scale soil maps for Great Britain has been allocated one of three figures (1, 2 or 4 kgN ha^{-1} yr^{-1}, representing low, medium and high rates of denitrification), based largely on soil drainage characteristics (Hall *et al.*, 1997). It should be noted that in the British context, gley soils are assumed to yield a higher rate of denitrification than peat soils.

Deposition dependent in-lake retention of N and S

The in-lake retention of acid anions is assumed to be a linear function of the net input of acidity. It is sequentially the final sink of acidity encountered by inputs which move through the catchment. Net in-lake retention of N is calculated as:

$$r\mathrm{N}_{ret} = \rho_N \left[\mathrm{N}_{dep} - f\mathrm{N}_{upt} - (1-r)(\mathrm{N}_{imm} + \mathrm{N}_{den})\right] \qquad \textit{(Equation 9)}$$

The "in-lake retention fraction" for nitrogen (ρ_N) is calculated from a kinetic equation accounting for water retention time:

$$\rho_N = \frac{S_N}{S_N + Q/r} \qquad \textit{(Equation 10)}$$

where S_N is the mass transfer coefficient for nitrogen, Q is runoff and *r* is the lake to catchment area ratio (Kelly *et al.*, 1987). A similar equation is used to calculate ρ_S, the "in-lake retention fraction" for sulphur.

Mid-range values from the published mass transfer coefficients for N and S (Kelly *et al.*, 1987, Dillon and Molot, 1990) were selected for this modelling study, with $S_N = 5.0\ \mathrm{m\ yr^{-1}}$ and $S_S = 0.5\ \mathrm{m\ yr^{-1}}$, in line with other national FAB applications in Scandinavia (Posch *et al.*, 1997, Henriksen, 1998). It should be noted that for stream sites, the lake:catchment ratio *r* is zero (the surface area of catchment streams is ignored in the calculation of *r*, since only in-lake processes are assumed to contribute to net retention of S and N). Hence both ρ_S and ρ_N are effectively zero in stream catchments.

Using the above methods to derive the terms for "internal" catchment processes, the charge balance provides those combinations of S and N deposition for which $\mathrm{AN}_{leach} = \mathrm{L}_{crit}$, thereby defining the critical load function (Figure 1). The constraints on the critical load function are given by:

$$\mathrm{CL}_{max}(\mathrm{S}) = \mathrm{L}_{crit} / (1-\rho_S) \qquad \textit{(Equation 11)}$$

$$\mathrm{CL}_{min}(\mathrm{N}) = f\mathrm{N}_{upt} + (1-r)(\mathrm{N}_{imm} + \mathrm{N}_{den}) \qquad \textit{(Equation 12)}$$

$$\mathrm{CL}_{max}(\mathrm{N}) = \mathrm{CL}_{min}(\mathrm{N}) + (\mathrm{L}_{crit} / (1-\rho_N)) \qquad \textit{(Equation 13)}$$

It is not possible to define a single value to represent the critical load of total acidity using the FAB model, since the acid anions sulphate and nitrate behave differently in the way they are transported with hydrogen ions; one unit of deposition of S will not have the same net effect on surface water ANC as an equivalent unit of N deposition. Equations 11-13 effectively define the critical deposition loads for S and N individually. $\mathrm{CL}_{max}(\mathrm{S})$ defines the critical load for sulphur when total N deposition is zero. This term is the equivalent to the SSWC model critical load for sulphur, modified slightly for the in-lake retention of a small proportion of inputs. When S deposition exceeds $\mathrm{CL}_{max}(\mathrm{S})$, the critical load is exceeded by S alone, regardless of the level of N deposition. The contribution of N deposition to an increase in exceedance over that resulting from S alone is determined by the FAB charge balance. $CL_{min}(N)$ defines the deposition of total N (NH_x + NO_x) at which terrestrial catchment processes effectively remove all N, so that deposition loads lower than $CL_{min}(N)$ result in no net leaching of nitrate. The terrestrial sinks for N are fixed by soil type and forest cover. An important assumption here is that all N deposition is transported through the terrestrial part of the catchment, i.e. in lake catchments there is negligible deposition directly onto the lake surface. $CL_{max}(N)$ defines the critical load for total N deposition when S deposition is zero. When total N deposition exceeds $CL_{max}(N)$ the critical load is exceeded by N deposition alone, although critical load exceedance may be further increased by S deposition.

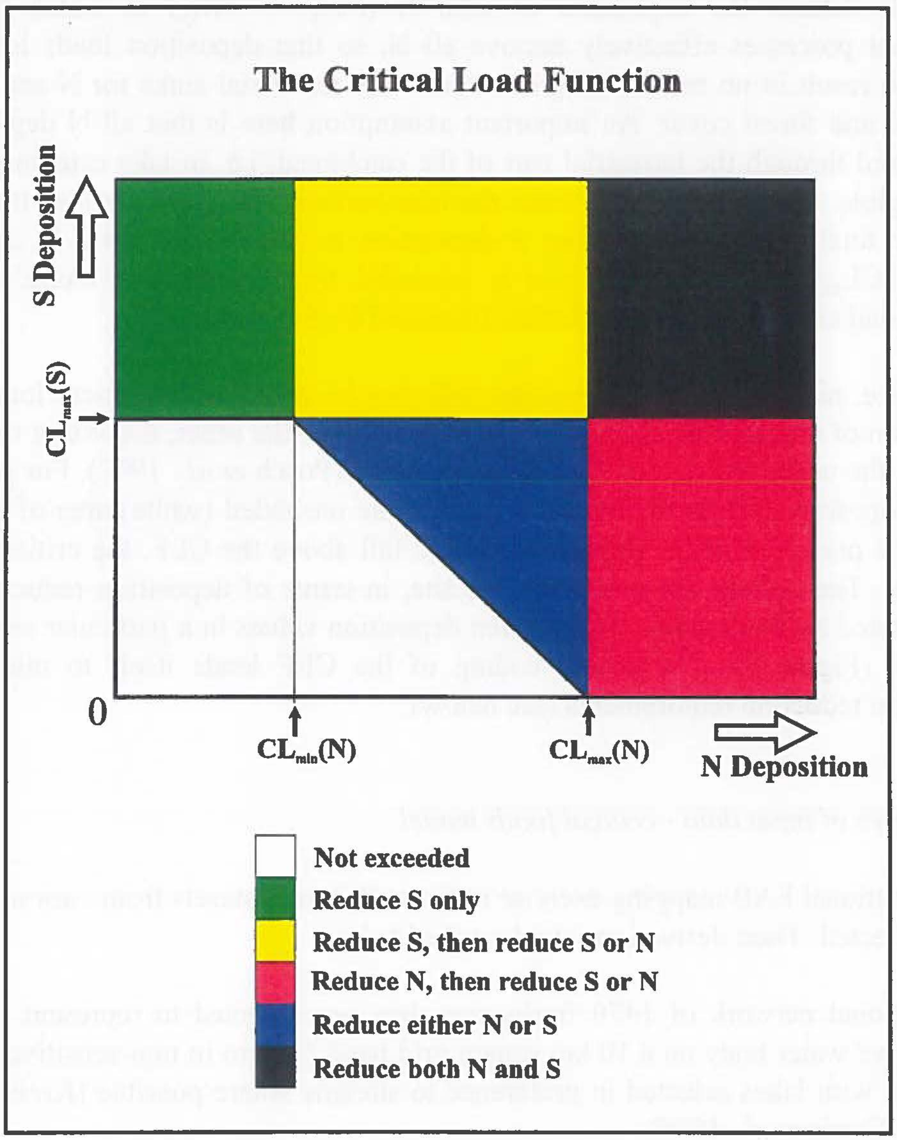
In practice, neither S nor N deposition will ever be zero, so the critical load for the deposition of one species is fixed by the deposition of the other, according to the line defining the unshaded area of the CLF in Figure 1 (Posch *et al.*, 1997). For pairs of S and N deposition values which are located in the unshaded (white) area of the CLF, the site is protected. If the deposition values fall above the CLF, the critical load is exceeded. The options for protecting the site, in terms of deposition reductions, are then dictated by the location of the given deposition values in a particular segment of the CLF (Figure 1). The colour coding of the CLF lends itself to mapping of deposition reduction requirements (see below).

2.2 Sources of input data - critical loads model

For the national FAB mapping exercise in Great Britain, datasets from various sources were collected. Their derivations are described below.

1. A national network of 1470 freshwater sites was selected to represent the most sensitive water body on a 10 km square grid basis (20 km in non-sensitive lowland areas), with lakes selected in preference to streams where possible (Kreiser *et al.*, 1993, Curtis *et al.*, 1996).
2. One-off dip samples were taken during autumn or early spring over the period 1992-94, and provided water chemistry which is assumed to approximate to flow-weighted mean chemistry (Forsius *et al.*, 1992). Chemical analysis was carried out according to the methodology of Harriman *et al.* (1990). These data were used to calculate L_{crit} with the SSWC model.
3. Site catchments and lake outlines were digitized from topographical maps at 1:25,000 scale, from which lake to catchment area ratio (r) was derived
4. Leaching fluxes from catchments were calculated using catchment area weighted runoff data from the 1km grid annual mean values for the period 1992-94.
5. Soil type and percentage cover were extracted for each catchment using digital catchment outlines and digital soils maps at 1:250,000 scale. The soils data were used to provide catchment weighted estimates of N_{imm} and N_{den} using the values suggested for each soil type in Hall *et al.* (1997).
6. Coniferous forest cover (f) was estimated for each catchment using digital catchment boundaries with the ITE land cover map (Fuller *et al.*, 1994) derived from satellite imagery at 25m pixel resolution.

Figure 1: The critical load function defined by the FAB model



The above datasets were used in the FAB charge balance to define the CLF for each of the 1470 freshwater sites, which can then be compared with sulphur and nitrogen deposition loads in order to assess spatial patterns of critical load exceedance and emission reduction requirements.

2.3 S and N deposition data

The national S and N deposition data used here are generated at the 20 km × 20km grid scale from measured and interpolated mean annual data in the UK (CLAG Deposition Fluxes, 1997, RGAR, 1997). For sulphur, total wet plus dry, seeder-feeder enhanced, non-marine values are used. For nitrogen, total N deposition is quantified as the sum of dry (NO_2+NH_3), cloud (NO_3^-, NH_4^+) and wet (NO_3^-, NH_4^+) deposition (CLAG Deposition Fluxes, 1997).

The deposition data are modelled from measurements made over the period 1992-1994, which corresponds with the period of freshwaters sampling. These are the most recently available data and are hereafter referred to as current deposition data (as opposed to datasets available for earlier periods).

It should be noted that the interpolated rainfall data used in the derivation of wet deposition are aggregated to the 20km × 20km scale, and the deposition data cannot be resolved to a finer scale than this (CLAG Deposition Fluxes, 1997). By contrast, the runoff data used to calculate catchment output fluxes from measured water chemistry are catchment-weighted 1km × 1km data. The implications of this difference in data resolution are discussed in Section 4 below.

3 Modelling results and predicted change

The charge balance which forms the basis of the FAB model and the "critical leaching of acid anions" (L_{crit}) term calculated with the SSWC model are based on assumed long-term, steady-state conditions. The FAB model outputs therefore indicate the status of freshwater bodies under a steady-state condition between deposition and catchment processes. In this respect, national maps based on FAB outputs using current deposition data cannot necessarily be expected to reflect the current chemical status of those freshwaters, because a steady-state cannot be assumed at present, especially with respect to nitrogen (Curtis *et al.*, 1998a). The outputs from the FAB model are effectively predictions of the chemical status of freshwaters under some future steady-state condition, and the most significant outputs in terms of changing chemistry are nitrate and ANC. Although there is a deposition-dependent sink for sulphur through in-lake retention processes, this generally accounts for a very small percentage of the S budget and so the difference between measured and predicted concentrations under a given deposition load should be very small. Deposition reduction requirements under current load and future conditions are a significant output in policy terms.

The FAB model outputs under the current deposition load are described below with respect to the most impacted areas as indicated by published critical load exceedance maps using the SSWC and diatom models (CLAG Freshwaters, 1995). The approximate locations of these regions are indicated in Figure 2.

3.1 Predicted increases in nitrate leaching

Most of the processes included in the FAB model are selected to determine the sustainable removal or retention rates of nitrogen. It is recognised that current nitrogen dynamics within catchments may be dictated by short term elevated rates of certain processes, notably soil immobilisation of N (Dise and Wright, 1995), but these transient processes must be excluded from the long term definition of critical loads (Curtis *et al.*, 1998a).

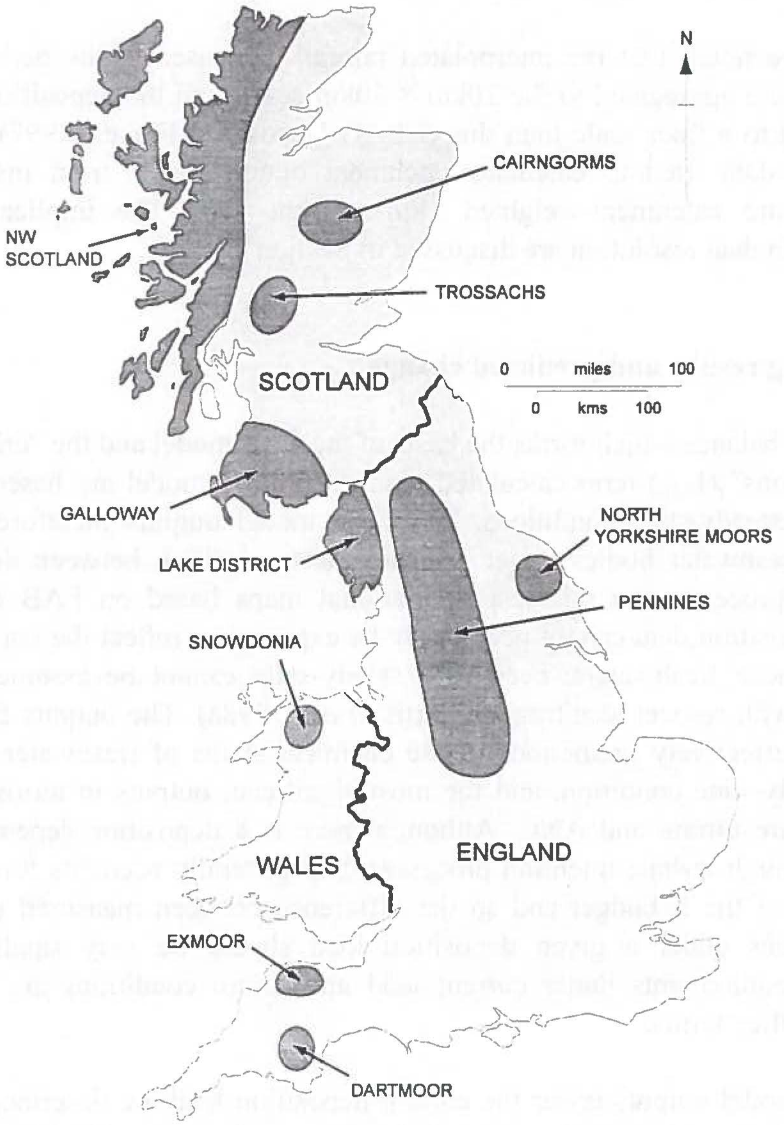


Figure 2: Selected regions of acid-sensitive upland waters in Great Britain referred to in the text

Current measured nitrate in British freshwaters shows strong regional patterns (Figure 3a). In northern Scotland, where S and N deposition levels are generally the lowest in Britain, most surface waters currently show negligible concentrations of nitrate (< 5 μeql^{-1}), often below detection limits. The highest levels of nitrate (> 100 μeql^{-1}) are found in lowland agricultural areas; eastern Scotland, south-west Wales and most of lowland (south-eastern) England. Water bodies in the acid-sensitive uplands of Britain tend to have nitrate concentrations which are intermediate between the near-zero levels of northern Scotland and the extreme levels in fertiliser impacted runoff in the lowlands (Allott *et al.*, 1995, INDITE, 1994). In these upland areas, the presence of high nitrate concentrations is generally attributable to atmospheric deposition, although simple input-output calculations in these areas still indicate a high level of nitrogen retention in catchments. An upland network of monitoring sites sampled monthly over two years indicated mean catchment retention levels of more than seventy-five percent for total inorganic nitrogen ($NH_4^+ + NO_3^-$), but less than fifty percent for nitrate alone (Curtis *et al.*, 1998a). This result implies the preferential retention of ammonium or its nitrification to nitrate.

The mass balance employed in the FAB model provides the potential, future nitrate leaching (N_{leach}):

$$N_{leach} = (1-\rho_N)\,(N_{dep} - fN_{upt} - (1-r)(N_{imm} + N_{den})) \qquad \textit{(Equation 14)}$$

This leaching flux of nitrate can be converted into a concentration if no change in annual runoff is assumed.

The FAB model predicts that nitrate leaching will greatly increase in all areas of Britain, except for the extreme north west of Scotland, under current deposition loads (Fig. 3b). The sampled sites in England are nearly all predicted to have nitrate concentrations of more than 100 μeql^{-1} upon reaching steady-state with current deposition levels, while most Welsh sites sampled would have nitrate concentrations in the range 50-100 μeql^{-1}. Nitrogen saturation and breakthrough is therefore predicted in most of the sampled upland catchments of England and Wales at some unspecified point in the future. In Scotland, a gradient of nitrate leaching is predicted from near zero concentrations in the extreme north-west, to values in the range 50-100 μeql^{-1} across most of the south.

The extreme national picture of future nitrate leaching (Fig. 3b) predicted by the FAB model results from the small size of available long-term nitrogen sinks in the model relative to current N deposition rates (Curtis *et al.*, 1998a). This map therefore closely reflects the theoretical distribution of nitrate concentrations resulting from the conversion of total N deposition flux into concentrations using runoff data. The realisation of these large increases in acid anion leaching would have serious knock-on effects on the ANC of water bodies in sensitive areas. In the non-sensitive lowlands, agricultural inputs of N are likely to be more significant than atmospheric inputs, but there will be no adverse impacts in terms of acidification in the surface waters draining these areas where eutrophication is more of a problem (INDITE, 1994).

3.2 Changes in ANC associated with acid anion leaching rates

If acid anion leaching does increase to a new steady-state level in the future, there will be an equivalent decrease in ANC associated with this change, and this is ultimately what the freshwater critical load models use to define exceedance. A site with a predicted ANC of less than 0 μeql^{-1} induced by a given acid deposition load is exceeding its critical load, even though current measured ANC may be greater than zero until steady-state is achieved.

Figure 4a shows that apart from a few isolated sites scattered around the country, water bodies with negative ANC values generally occur in the recognised areas of acidification (see Fig. 2); Galloway in Scotland, the Lake District, Pennines and North Yorkshire Moors of northern England, and the uplands of Wales. The great majority of fresh waters have a positive ANC, although in north west Scotland there are very few sites with an ANC greater than 20 μeql^{-1}, indicating a region of extreme sensitivity to acidification. In sites with positive but low ANC, the impact of increased acid anion leaching is likely to be most significant in terms of causing critical load exceedance.

The charge balance of the FAB model can be employed to calculate the potential, future ANC at a site under a constant deposition load. Future nitrate leaching is derived as above, and sulphate leaching (S_{leach}) is provided by subtracting the in-lake retention component from deposition inputs:

$$S_{leach} = (1 - \rho_S)\, S_{dep} \qquad \text{(Equation 15)}$$

The SSWC model assumes that the only permanent, sustainable source of base cations is provided by weathering, so that despite current elevated rates of base cation leaching through cation exchange processes with acid inputs, base cation concentrations under a constant deposition load and runoff will decline to the value of $[BC]_0^*$ (see Section 2.1 above). The potential, future ANC concentration ($[ANC_{pot}]$) is then provided by the difference between future base cation and acid anion concentrations:

$$[ANC_{pot}] = [BC]_0^* - (S_{leach} + N_{leach})/Q \qquad \text{(Equation 16)}$$

where S_{leach} and N_{leach} are derived as in Equations 14-15 above.

The predicted increase in acid anion leaching under current deposition loads will lead to a decrease in ANC at many sites if no emissions abatement is implemented (Figure 4b). In general, for England and Wales the reductions in ANC predicted by the FAB model are most apparent at sites with measured ANC values of less than zero (Fig. 4a), i.e. at sites which are already acidified. There is effectively a "consolidation" of acidified regions, with an increased spatial distribution of acidified sites as well as greater impacts at already acidified sites. In Wales, the region of acidification expands in area from north and mid-Wales to most of the uplands in the centre and south of the country. In parts of central and northern Scotland, small increases in nitrate leaching, combined with extremely sensitive, dilute water bodies, will lead to a switching of ANC from positive to negative values, potentially with serious effects on the fisheries there. Less significant is the further reduction in ANC throughout the Pennine region; fish are already absent from many water bodies there which have been severely acidified for many years.

3.3 Deposition reduction requirements according to the FAB model

While the prediction of a negative ANC with the FAB model equates to a critical load exceedance, the utility of the FAB model lies also in the identification of the acid species which needs to be reduced in order to protect the site. If each site is colour coded according to its location on the critical load function (CLF - see Figure 1) then a national map of deposition reduction requirements can be produced (Figure 5).

Comparison of current deposition data with the critical load function indicates a regional pattern in the relative importance of S and N deposition. Many Scottish sites exceeding their critical loads require a mandatory reduction in S deposition in order to attain non-exceedance, i.e. the critical loads are currently exceeded by sulphur alone (Figure 5). At most of the remaining exceeded sites in Scotland, reductions in S would provide sufficient protection, although N deposition could also be reduced to achieve the same outcome. It would therefore be possible to protect the majority of the Scottish sites through abatement of S emissions alone, without the need for recourse to N reductions. The only area of Scotland where N reductions are compulsory to protect freshwaters is the highly impacted Galloway region (Fig. 2).

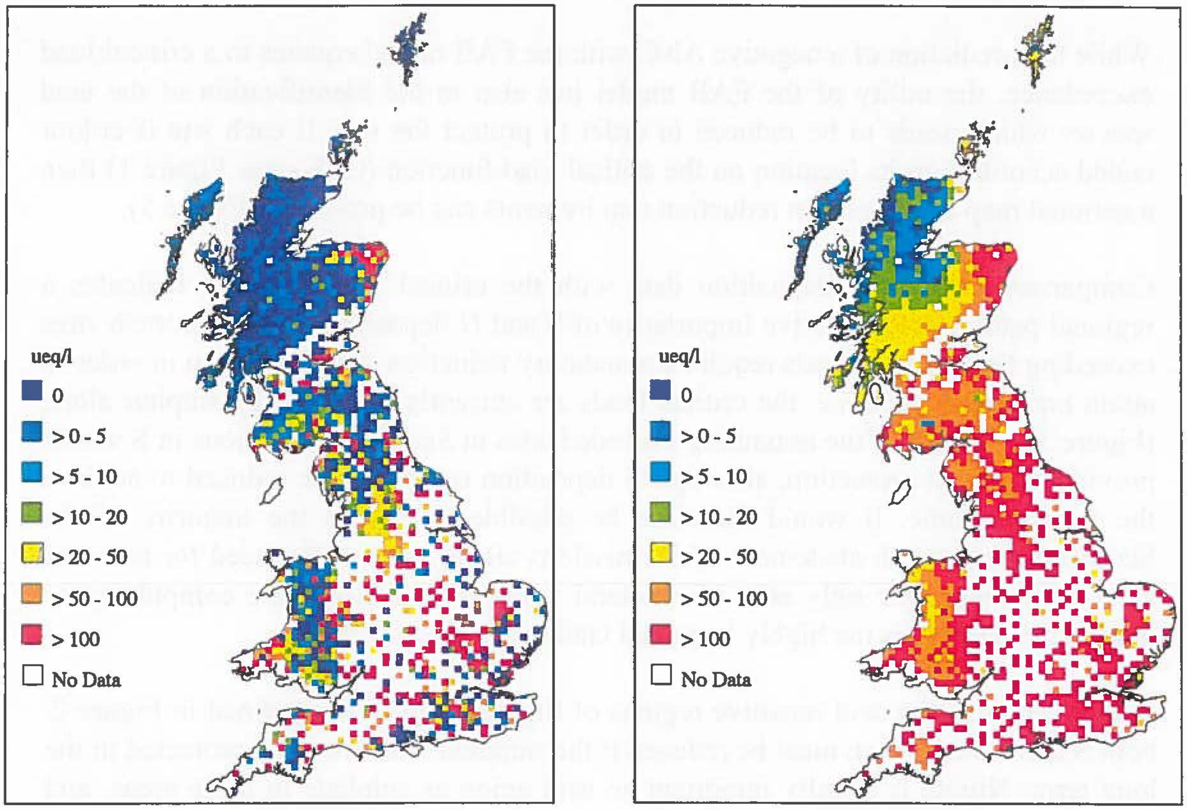
In large areas of the acid sensitive regions of England and Wales defined in Figure 2, both S and N deposition must be reduced if the sampled sites are to be protected in the long term. Nitrate is equally important an acid anion as sulphate in these areas, and the control of sulphur emissions alone, even with (unfeasible) reductions to zero, would be insufficient to protect these sites from acidification. The implication is that currently agreed international commitments to reduce S emissions under the Second Sulphur Protocol (UNECE, 1994) will be of limited benefit to the most sensitive freshwaters in Britain unless N deposition is also reduced.

The number of freshwater sites falling into each deposition reduction category identified on the CLF for the current deposition levels indicates the requirement for emissions reductions strategies (Table 1).

Of the sampled population of 1470 lake and stream sites, 391 sites (27%) exceed their critical loads under current deposition levels. In terms of the proportion of water bodies with critical load exceedance, Wales is the most impacted, with 46% of sampled sites exceeded. Scotland and England have greater numbers of exceeded sites in absolute terms (Table 1), but smaller proportions with 23% and 26% exceeded respectively. Note that these percentages refer to sampled sites, not the whole population of water bodies in these countries.

The proportions of sites affected by S or N deposition, or both, are given in Table 2, where the regional nature of deposition effects is exemplified. In England, 75% of exceeded sites require mandatory reductions in S deposition in order to be protected from acidification beyond the critical chemical value (below ANC = 0 $\mu eq l^{-1}$). However, most of these sites also require reductions in N deposition; 68% of exceeded sites would still be exceeded if S or N deposition were reduced to zero and the other remained constant. In England, therefore, nitrogen presents an equal problem to sulphur, at least in terms of numbers of sites affected. Expected reductions in S

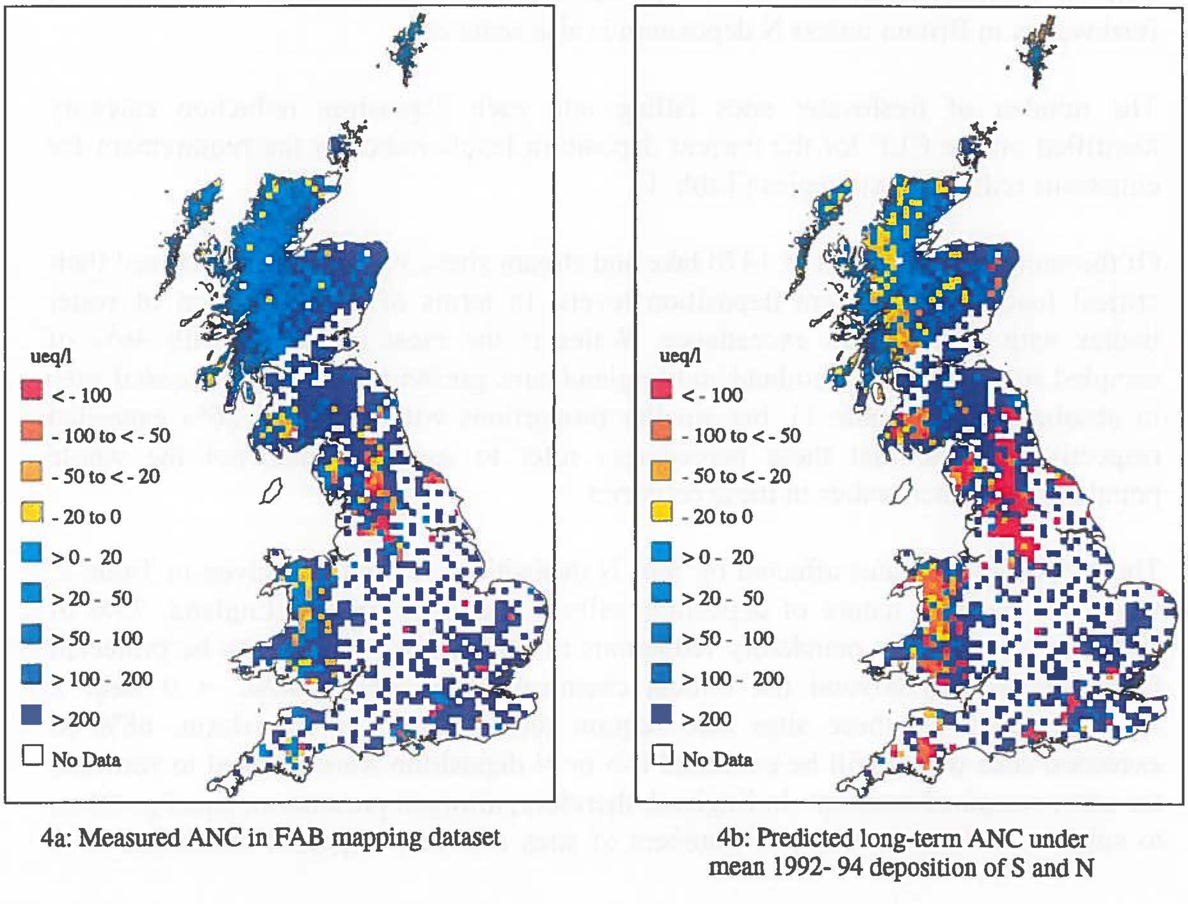
Figure 3: Measured and modelled nitrate concentrations in the FAB mapping dataset



3a: Measured nitrate in FAB mapping dataset

3b: Predicted long-term nitrate leaching under mean 1992- 94 deposition load of S and N

Figure 4: Measured and modelled ANC in the FAB mapping dataset



4a: Measured ANC in FAB mapping dataset

4b: Predicted long-term ANC under mean 1992- 94 deposition of S and N

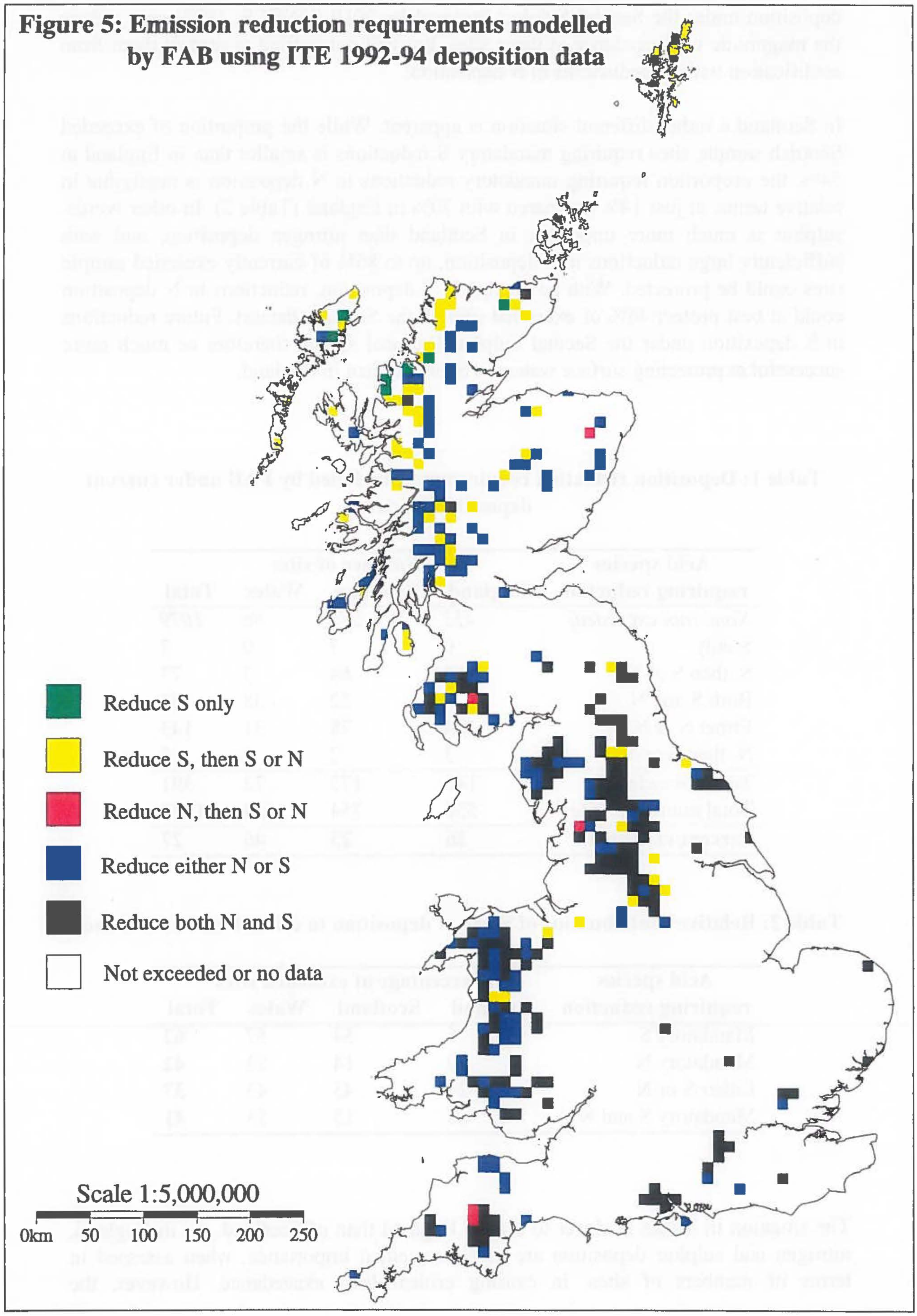


Figure 5: Emission reduction requirements modelled by FAB using ITE 1992-94 deposition data

deposition under the Second Sulphur Protocol by 2010 (UNECE, 1994) may reduce the magnitude of exceedance at these sites, but will not suffice to protect them from acidification without reductions in N deposition.

In Scotland a rather different situation is apparent. While the proportion of exceeded Scottish sample sites requiring mandatory S reductions is smaller than in England at 54%, the proportion requiring mandatory reductions in N deposition is negligible in relative terms, at just 14% compared with 70% in England (Table 2). In other words, sulphur is much more important in Scotland than nitrogen deposition, and with sufficiently large reductions in S deposition, up to 86% of currently exceeded sample sites could be protected. With no change in S deposition, reductions in N deposition could at best protect 46% of exceeded sites in the Scottish dataset. Future reductions in S deposition under the Second Sulphur Protocol should therefore be much more successful at protecting surface waters in Scotland than in England.

Table 1: Deposition reduction requirements modelled by FAB under current deposition loads

Acid species requiring reduction	**Number of sites** **England**	**Scotland**	**Wales**	**Total**
None (not exceeded)	*412*	*581*	*86*	***1079***
S only	0	7	0	**7**
S, then S or N	10	64	3	**77**
Both S and N	99	22	38	**159**
Either S or N	34	78	31	**143**
N, then S or N	3	2	0	**5**
Total exceeded	146	173	72	**391**
Total number of sites	558	754	158	**1470**
Percent exceeded	**26**	**23**	**46**	**27**

Table 2: Relative contributions of S and N deposition to critical load exceedance

Acid species requiring reduction	**Percentage of exceeded sites** **England**	**Scotland**	**Wales**	**Total**
Mandatory S	75	54	57	**62**
Mandatory N	70	14	53	**42**
Either S or N	23	45	43	**37**
Mandatory S and N	68	13	53	**41**

The situation in Wales is closer to that of England than of Scotland. As in England, nitrogen and sulphur deposition are of almost equal importance, when assessed in terms of numbers of sites, in causing critical load exceedance. However, the proportion of exceeded sites at which reductions in both S and N deposition are required is smaller, at 53% compared with 68% in England (Table 2). Future reductions in S deposition could at best protect 47% of currently exceeded Welsh sample sites without any reduction in N deposition.

4 Discussion

The results of the national model application have to be considered in the context of the uncertainties associated with the model structure, the catchment datasets and the deposition data used.

4.1 Uncertainties associated with critical load models for freshwaters

One of the major uncertainties associated with the SSWC model relates to the use of a single chemical sample for the derivation of the F-factor and L_{crit} (see Section 2.2 above), when these would ideally be based on annual mean chemistry. The size of the water sampling programme dictated that only a one-off spot sample could be collected for water chemistry, but it is known that there are significant seasonal variations in water chemistry in most freshwaters. In a network of upland lakes monitored monthly over two years, it was found that the calculated value of L_{crit} could vary by almost an order of magnitude, depending on the date of the chemical sample used (Curtis *et al.*, 1998b). The freshwaters sampling period was generally restricted to the late spring and autumn in order to minimise the risk of sampling under extreme chemical conditions, but the representativeness of the sample is unknown.

The input parameters to the FAB model, where limited empirical data have been used to specify various process rates at the national scale, will have associated errors which can only be reduced by further empirical study and revision of default values.

The nitrogen uptake term (N_{upt}) incorporates two sources of uncertainty; the estimate of forest cover from satellite imagery and the single rate of N uptake selected for all forest areas. The accuracy of the land cover data has been estimated as 80-85% (Fuller *et al.*, 1994), but the spatial resolution (at best a 25m grid) of the data will introduce uncertainty into catchment scale estimates. The land cover data do not distinguish between tree species, just between deciduous and coniferous. It is assumed that all coniferous forest is harvested. The selected default value for N_{upt} lies in the middle of a published range for just one species (Sitka spruce) so there will variations in N_{upt} relating to species, yield class, location and harvesting practice.

All the above uncertainties in the derivation of N_{upt} are difficult to quantify, but the affected proportion of the mapping dataset will be small; only 12% of the 1470 catchments have an estimated coniferous forest cover of more than a tenth, and only two percent of catchments have more than half of their area afforested with conifers (CLAG, unpublished data).

The denitrification component of the FAB model is another source of uncertainty. The default terms used for British soil types are literature based estimates (Hall *et al.*, 1997), and very few data are available for moorland sites in Britain. Current research efforts are therefore directed towards the measurement of denitrification rates from moorland soils in both the field and the laboratory.

Despite the uncertainties in both the N uptake and denitrification terms, the available data (Emmett and Reynolds, 1996) suggest that these two processes alone are unlikely to account for the very high rates of N retention or removal observed at a network of British upland catchments sampled monthly over two years (Curtis *et al.*, 1998a, 1998b). There is evidence to suggest that N immobilisation in soil biomass may occur at elevated rates until N saturation occurs, i.e. until some other essential resource is limiting (Aber *et al.*, 1989), which may be reflected in increased soil carbon:nitrogen ratios and nitrate leaching in the future (Dise and Wright, 1995). While this process could explain the very high rates of N retention currently observed in many upland catchments, it poses a problem in the definition of critical loads, whereby a long-term steady-state is assumed.

The approach adopted at the European level is to utilise the long-term estimates of soil N immobilisation obtained from chronosequence studies (UBA, 1996) which provide a much smaller figure (0.5 – 1.0 kgN ha^{-1} yr^{-1}) for immobilisation than current catchment budgets would indicate. Given the sparsity of data on the immobilisation process. and the relatively low rates of net N uptake and denitrification suggested by more readily available data, it is assumed that there is discrepancy between current high immobilisation rates and the very low long-term rates employed in the FAB model. This difference could largely account for the very high rates of nitrate leaching predicted in the future, i.e. it is the assumed decline in future immobilisation rates which dominates the long-term N budgets. However, it is not known what the sustainable rate of soil N immobilisation could be when soil processes are operating at steady-state with respect to elevated N inputs, and there is clearly a major research issue to be addressed.

One specific source of error within the FAB model is the assumption that all acid deposition to a catchment passes through the terrestrial system and is thereby exposed to the various soil and vegetation sinks which act to remove nitrogen. Direct deposition to the lake surface is assumed to be negligible, but for certain water bodies in areas of very low relief, for example in the Flow Country of northern Scotland, the lake surface may form a major fraction of the total catchment area, in some cases as high as forty percent. While such cases are rare, the critical loads calculated with the FAB model will be significant overestimates for these sites.

The actual chemical trajectory of water bodies cannot be modelled by FAB because of the interactions of dynamic processes, including changes in N uptake rates through the forest growth cycle (Emmett *et al.*, 1993) and the gradual N saturation of terrestrial catchment ecosystems (Dise and Wright, 1995) in the context of declining inputs of both S and N based acidity. The timing of the anticipated changes in water chemistry cannot therefore be estimated, but they are assumed to occur as steady-state is achieved over the long term.

4.2 Uncertainties associated with deposition data

There are several potential sources of uncertainty associated with the deposition data used, including interpolation (kriging) error, uncertainties in dry deposition velocity and precipitation amount, and uncertainties associated with seeder-feeder enhancement of wet deposition at scales smaller than the 20 × 20 km grid employed (CLAG Deposition Fluxes, 1997). The uncertainty associated with deposition inputs into a 20km grid cell has been estimated as ± 40% for total sulphur over much of the country, rising to ± 60% towards the north and west of Britain (CLAG Deposition Fluxes, 1997). The uncertainties in N deposition fluxes to a 20 × 20 km grid square, and those associated with local topographical and land cover variations within a 20 × 20 km area, are unknown.

Another uncertainty relates to the issue of data resolution. While FAB is a catchment based model, with catchment specific estimates of soil and vegetation cover, the deposition and runoff data are not catchment specific. Mean deposition estimates are produced on a 20 × 20 km grid, while the mean total catchment area for sites in the mapping database is 2.4 km^2. The rainfall data used in the derivation of wet deposition are 20 × 20 km mean data, while inspection of the 1 × 1 km runoff data shows that values can vary by a factor of two or more within any 20 × 20 km grid square. Given that one of the original selection criteria for mapping sites was that all other things being equal, the lake or stream at the greatest altitude was selected, and given that seeder-feeder enhancements to deposition can occur with increasing altitude (Dore *et al.*, 1992), it is likely that many catchments lie above the mean altitude for a 20 × 20 km square and that wet deposition may therefore be underestimated. Critical load exceedance may therefore be underestimated at some sites.

The mismatch between resolution of runoff data (1 km resolution, catchment weighted mean values) and rainfall data (average 20 km resolution data) also presents an issue in terms of catchment budgets. It is assumed that the 1 km resolution, catchment weighted runoff data provide the most accurate figure for surface water fluxes from sample catchments. i.e. are the best available data at the national scale. Current deposition models are not yet able to reproduce a greater resolution than 20 × 20 km estimates. but this should not preclude the use of best available runoff data for calculating export fluxes. This approach is comparable with that adopted for modelling soils critical loads, whereby critical loads and exceedances are derived at a 1 × 1 km resolution despite the availability of deposition data only at a much coarser resolution (CLAG Mapping and Modelling, 1996).

4.3 Interpretation of FAB model outputs

Interpretation of the chemical predictions and deposition reduction requirements generated by the FAB model requires an understanding of several key factors:

1. the chemical consequences of a critical load exceedance and the link with deposition reduction requirements,

2. the unknown timescale of acidification damage,
3. the context of a predicted chemical change, and
4. the population of sites in the mapping dataset.

These issues are discussed in turn below.

The magnitude of critical load exceedance and deposition reduction requirements

A critical load exceedance implies that at some unspecified time in the future, the critical chemical criterion will not be met. In this model application, exceedance therefore indicates that annual mean ANC will not be maintained above 0 μeql^{-1} in the long term. The magnitude of critical load exceedance determines the ultimate, steady-state ANC of the impacted water body (all other things being equal) and by conversion of the excess acidity flux into a concentration of acid anions, the future ANC can be predicted (Fig. 4b).

In previous applications of steady-state critical load models for sulphur to the British freshwaters dataset using the SSWC (Henriksen *et al.*, 1992) and diatom (Battarbee *et al.*. 1996) models, the assumption that the sulphate anion moved unimpeded through catchments meant that all excess acid deposition (expressed as critical load exceedance) was causing acidification (CLAG Freshwaters, 1995). The amount of exceedance, expressed as equivalents of acidity, was the amount by which S deposition had to be reduced in order to protect the site. The same is not true for the process-oriented FAB model in which catchment processes affect the fluxes of acid anions.

The national FAB map of deposition reduction requirements (Fig. 5) does not indicate the magnitude of critical load exceedance in terms of a deposition flux of acidity, because this notional figure cannot be interpreted directly as the size of the deposition reduction requirement. The reduction requirement for S or N deposition will inevitably be greater, in terms of equivalents of acidity, than the amount by which the critical load is exceeded. because of the catchment processes which retain a proportion of the inputs. For example, if in-lake retention of S is estimated as 10% of inputs, then only 90% of a reduction in S deposition will be reflected in a decrease in sulphate concentration in the lake outflow. Each unit of reduction in S deposition will therefore provide only 0.9 units of reduction in exceedance. The situation for N is more complex because of the number of potential sinks for N, which may operate at fixed rates or be deposition dependent, but will be more significant, given the much greater proportions of N retention in catchments, and hence the much smaller benefits in terms of reduced acid anion leaching relative to an equivalent reduction in S.

The only exceptions to the above circumstances are stream sites for which N deposition is less than $CL_{min}(N)$ (i.e. all N deposition is retained in the terrestrial catchment). In these cases, the absence of in-lake retention processes means that S retention is zero so that a numerical exceedance of S deposition reflects the deposition reduction requirement for S. There are no such sites in the mapping dataset used here;

only seven sites, all standing waters in Scotland, are exceeded with zero nitrate leaching.

Because of the inter-dependence of S and N deposition in causing critical load exceedance, the FAB model cannot provide an absolute requirement for deposition reductions in either S or N beyond the upper deposition thresholds of $CL_{max}(S)$ and $CL_{max}(N)$ (Fig. 1). Where the deposition load of either species lies below these thresholds, the reduction requirement for one cannot be specified without reference to the other. In other words, while the FAB model output indicates the options for reducing acid deposition in terms of S or N, it cannot provide independent figures for either. The utility of the model therefore lies in deposition scenario assessment, whereby the effect of given combinations of S and N deposition can be assessed to determine whether they provide adequate protection to the freshwater sites of concern. One such application of the model is described in Curtis *et al.* (1998c) where the levels of protection afforded by three deposition scenarios (baseline, planned and potential) are compared.

<u>The timing of acidification damage</u>

It has already been stated that the major outputs from the FAB model are predictions of future chemical status when catchment processes are at steady-state with deposition inputs, and that the timing of future change cannot be provided by the model. It is therefore important to note that a state of critical load exceedance does not necessarily mean that the affected water body has already been acidified or even significantly affected as yet by the excess acid deposition. If the critical load of a site is currently exceeded, then the critical chemical threshold will be crossed at some unspecified point in the future, i.e. *the current deposition load cannot be sustained if the site is to be protected.* In both the SSWC and FAB models, critical load exceedance is therefore not a function of current damage, but of *potential* future damage. The actual current state of a water body for which the critical load is exceeded is determined by such factors as deposition history (total cumulative acid load) and catchment characteristics like soil type and land cover, so that only dynamic models like MAGIC which incorporate such factors can predict the timing of acidification to a given chemical state (e.g. Jenkins *et al.*, 1997).

The FAB model indicates that under prevailing deposition levels at the time of the CLAG lakes survey, 27% of sampled sites were exceeding their critical loads. For the reasons stated above, this does not necessarily mean that this proportion of sampled sites are currently damaged; some of them will have already acidified, while others will not as yet be adversely affected. While the time period over which damage will occur cannot be assessed with steady-state models, there is a link between the rate at which acidification might occur (or have already occurred) and the magnitude of critical load exceedance, because the rate of acidification processes (e.g. soil base cation depletion, nitrogen saturation) will be at least partly dependent on the deposition load of S or N. It is therefore evident that sites with the greatest critical load exceedance are the most likely to be damaged already, and are the sites where deposition reductions will probably be most urgently required. The greatest exceedance values are reflected in the most negative predicted ANC values in Figure 4b.

Interpreting the predicted chemical status

Another key point in the interpretation of critical loads and exceedances is that they refer to *long-term* steady-state. The chemical data used to derive critical loads are assumed to approximate to flow-weighted annual mean values. Critical loads are set relative to a critical chemical criterion, in this case a flow-weighted annual mean ANC of 0 μeql^{-1}. A critical load exceedance or model prediction therefore refers to annual mean conditions and not to any spot chemical value. However, this should not be interpreted as meaning that at steady-state, in any one year the annual mean ANC of an exceeded water body will be less than 0 μeql^{-1}. The temporal resolution of predictions is greatly limited by the incorporation of nitrogen cycling processes which are averaged on a decadal timescale.

The nitrate and ANC concentrations predicted by the FAB model (Figs. 3b and 4b) assume no change in water fluxes and represent long-term annual mean conditions. No account is taken of seasonal chemical variability or the effects of short-term episodicity (e.g. Curtis *et al.*, 1998b). Furthermore, taking the example of N uptake in forests, a harvesting cycle of forty years is assumed (Emmett and Reynolds, 1996), while it is recognised that throughout this period, actual uptake rates will be largely dependent on forest age (Emmett *et al.*, 1993). In this respect, the FAB model predictions of chemistry are assumed to represent a forty year annual mean. It is therefore currently impossible to validate this aspect of the model, because no data are available for such a long time period.

Extrapolation of exceedance map to other freshwater sites

Since the chosen freshwaters sampling strategy focused on the most sensitive sites, rather than a randomly selected representative subsample, the results of the modelling exercise cannot be extrapolated to the whole population of British water bodies. By definition, the selection of the most sensitive site in each 10 × 10 km grid square should mean that where the selected site is protected, the associated water bodies in the same grid square are also protected because they are less sensitive and will therefore have higher critical loads. This uncertainty was quantified by Curtis *et al.* (1995) who found that in SSWC model applications to the British freshwaters mapping dataset, the most sensitive site in a 10 × 10 km grid square was correctly identified in one third of cases, while the selected site correctly represented the most sensitive critical load class of water bodies in the grid square in two thirds of cases. The implication here is that in around two thirds of mapped grid squares where critical loads are exceeded, there may be water bodies experiencing an even greater critical load exceedance than the mapped site.

It is not possible to further quantify how many of the associated sites in a grid square are also exceeded, because there are no data to link the critical loads of the general population of water bodies to those of the sampled sites. Neither is it possible to quantify the number of sites which are not exceeded, but which may lie in a grid square where a more sensitive, unsampled site would be exceeded.

5 Conclusions

The national application of the FAB model to a dataset of 1470 British freshwaters indicates that more than a quarter of sampled sites may be damaged in the long term if the deposition of acidity is not reduced. There is a distinct regional pattern in the relative importance of S or N deposition in causing acidification.

The uplands of northern England and Wales will experience the most severe acidification, mostly through increases in nitrate leaching. Ironically, many of the sites predicted to be most seriously impacted in the Pennine region are already acidified and fishless, so any further decrease in ANC cannot affect the (absent) target organism, brown trout. Potentially more serious is the decline in ANC predicted for many sites in upland Wales and the Lake District of northern England, where sites are currently less acidic and there will be more to lose in terms of fisheries. Perhaps most striking is the decrease in ANC to less than 0 μeql^{-1} in sites across large parts of western Scotland, because these sites currently have positive ANC values and this region has not yet shown evidence of serious acidification damage to fisheries (Harriman *et al.*, 1995). Unlike England and Wales, the future acidification of Scottish freshwaters is determined largely by S deposition.

While previous international efforts have been directed towards a strategy for the control of S emissions, the FAB model indicates that S emissions reduction alone will be insufficient to protect sites in much of upland England and Wales because of the magnitude of N deposition. Only the Scottish sample sites could be protected by S reductions alone, depending on the deposition levels attained. There is an evident need for reductions in N deposition across most of the country if any benefits from future decreases in S deposition are to be realised.

The FAB model cannot provide the timescales over which acidification damage might occur, but this national application does provide a coherent, regional picture of the potential magnitude of change in sampled lakes and streams, and provides a graphic illustration of where sulphur or nitrogen deposition, individually or in combination, must be reduced in order to protect these sensitive ecosystems.

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References

Aber, J.D., Nadelhoffer, K.D., Steudler, P. and Melillo, J.M. (1989) Nitrogen saturation in Northern forest ecosystems. *BioScience* **39 (6)**, 378-386.

Allott, T.E.H., Curtis, C.J., Hall, J., Harriman, R. and Battarbee, R.W. (1995) The impact of nitrogen deposition on upland freshwaters in Great Britain: a regional assessment. *Water, Air and Soil Pollution* **85(2)**, 297-302.

Battarbee, R.W., Allott, T.E.H., Juggins, S., Kreiser, A.M., Curtis, C. and Harriman, R. (1996) Critical loads of acidity to surface waters - an empirical diatom-based palaeolimnological model. *Ambio* **25(5)**, 366-369.

Brakke, D.F., Henriksen, A. and Norton, S.A. (1990) A variable F-factor to explain changes in base cation concentrations as a function of strong acid deposition. *Verh. Internat. Verein. Limnol.* **24**, 146-149.

Bull, K.R. (1995) Critical loads - possibilities and constraints. *Water, Air and Soil Pollution* **85 (1)**, 201-212.

CLAG (1994) *Critical Loads of Acidity in the United Kingdom.* UK Critical Loads Advisory Group, Summary Report to the Department of the Environment, February 1994. ITE, Penicuik, 61pp.

CLAG Deposition Fluxes (1997) *Deposition fluxes of acidifying compounds in the United Kingdom.* Critical Loads Advisory Group, Sub-group report on Deposition Fluxes. ITE, Penicuik, 45pp.

CLAG Freshwaters (1995) *Critical Loads of Acid Deposition for United Kingdom Freshwaters.* Critical Loads Advisory Group, Sub-group report on Freshwaters. ITE, Penicuik, 80pp.

CLAG Mapping and Modelling (1996) *Mapping and modelling environmental acidification in the United Kingdom.* Critical Loads Advisory Group, Sub-group report on mapping and modelling. ITE, Penicuik, 28pp.

Curtis. C.J., Allott, T.E.H., Battarbee, R.W. and Harriman, R. (1995) Validation of the UK critical loads for freshwaters: site selection and sensitivity. *Water, Air and Soil Pollution* **85(4)**, 2467-2472.

Curtis. C.J., Allott, T.E.H., Battarbee, R.W., Harriman, R., and Hall, J. (1996) *Screening and validation of the empirical maps for UK freshwater critical loads.* ECRC Research Papers No. 12, University College London, 120pp.

Curtis. C.J., Allott, T.E.H., Reynolds, B. and Harriman, R. (1998a) The prediction of nitrate leaching with the first-order acidity balance (FAB) model for upland catchments in Great Britain. *Water, Air and Soil Pollution* **105**, 205-215.

Curtis. C.J., Harriman, R., Allott, T.E.H. and Kernan, M. (1998b) *Water chemistry and critical load modelling at a network of moorland lake and reservoir sites in the British uplands: 2 Year Data Report (1996-97).* ECRC Research Report No. 50, University College London, 181pp.

Curtis, C.J., Whyatt, J.D., Metcalfe, S.E., Allott, T.E.H. and Harriman, R. (1998c) *Assessing the impact of international emissions reduction scenarios to combat the acidification of freshwaters in Great Britain with the First-order Acidity Balance (FAB) model and the Hull Acid Rain Model (HARM).* ECRC Research Paper No. 17, University College London, 22pp.

Dillon, P.J. and Molot, L.A. (1990) The role of ammonium and nitrate retention in the acidification of lakes and forested catchments. *Biogeochemistry* **11**, 23-43.

Dise, N.B. and Wright, R.F. (1995) Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management* **71**, 153-161.

Dore, A.J., Choularton, T.W., Brown, R. and Blackall, R.M. (1992) Orographic rainfall enhancement in the mountains of the Lake District and Snowdonia. *Atmospheric Environment* **264 (3)**, 357-371.

Emmett, B.A., Reynolds, B., Stevens, P.A., Norris, D.A., Hughes, S., Görres, J. and Lubrecht, I. (1993) Nitrate leaching from afforested Welsh catchments - interactions between stand age and nitrogen deposition. *Ambio* **22 (6)**, 386-394.

Emmett, B.A. and Reynolds, B. (1996) Nitrogen critical loads for spruce plantations in Wales: is there too much nitrogen? *Forestry* **69 (3)**, 205-214.

Forsius, M., Kämäri, J. and Posch, M. (1992) Critical loads for Finnish lakes: comparison of three steady-state models. *Environmental Pollution* **77**, 185-193.

Fuller, R.M., Groom, G.B. and Jones, A.R. (1994) The Land Cover Map of Great Britain: an automated classification of Landsat Thematic Mapper data. *Photogrammetric Engineering and Remote Sensing* **60**, 553-562.

Hall, J., Hornung, M., Freer-Smith, P., Loveland, P., Bradley, I., Langan, S., Dyke, H., Gascoigne, J. and Bull, K. (1997) *Current status of UK critical loads data - December 1996.* ITE Monks Wood, UK, 22pp plus appendices.

Harriman, R., Gillespie, E., King, D., Watt, A.W., Christie, A.E.G., Cowan, A.A. and Edwards, T. (1990) Short-term ionic responses as indicators of hydrochemical processes in the Allt a'Mharcaidh catchment, western Cairngorms, Scotland. *Journal of Hydrology* **116**, 267-285.

Harriman, R. and Christie, A.E.G. (1995) Estimating critical loads for biota: the steady-state water chemistry (Henriksen) model. In: CLAG Freshwaters, *Critical Loads of Acid Deposition for United Kingdom Freshwaters.* Critical Loads Advisory Group, Sub-group report on Freshwaters. ITE, Penicuik, pp.7-8.

Harriman, R., Bridcut, E.E. and Anderson, H. (1995) The relationship between salmonid fish densities and critical ANC at exceeded and non-exceeded stream sites in Scotland. *Water, Air and Soil Pollution* **85(4)**, 2455-2460.

Henriksen, A. (1984) Changes in base cation concentration due to freshwater acidification. *Verh. Internat. Verein. Limnol.* **22**, 692-698.

Henriksen, A. (1998) *Application of the first-order acidity balance (FAB) model to Norwegian surface waters.* Report SNO 3809-98, Norwegian Institute for Water Research (NIVA), Oslo, Norway, 33 pp.

Henriksen, A., Lien, L., and Traaen, T.S. (1990) Critical loads for surface waters – Chemical criteria for inputs of strong acids. Report 22/1990, Norwegian Institute for Water Research (NIVA), Oslo, Norway.

Henriksen, A., Kämäri, J., Posch, M. and Wilander, A. (1992) Critical loads of acidity: Nordic surface waters. *Ambio* **21(5)**, 356-363.

Henriksen, A., Hindar, A., Hessen, D. and Kaste, Ø. (1997) Contribution of nitrogen to acidity in the Bjerkreim River in Southwestern Norway. *Ambio* **26(5)**, 304-311.

INDITE (1994) *Impacts of nitrogen deposition in terrestrial ecosystems. Report of the United Kingdom Review Group on Impacts of Atmospheric Nitrogen.* UK Department of the Environment, London, 110pp.

Jenkins, A., Renshaw, M., Helliwell, R., Sefton, C., Ferrier, R. and Swingewood, P. (1997) *Modelling surface water acidification in the UK.* Report No. 131, Institute of Hydrology, Wallingford, UK, 54pp.

Kämäri, J., Amann, M., Brodin, Y.-W., Chadwick, M.J., Henriksen, A., Hettelingh, J.-P., Kuylenstierna, J., Posch, M. and Sverdrup, H. (1992) The use of critical loads for the assessment of future alternatives to acidification. *Ambio* **21(5)**, 377-386.

Kämäri, J., Forsius, M. and Posch, M. (1993) Critical loads of sulfur and nitrogen for lakes II: regional extent and variability in Finland. *Water, Air and Soil Pollution* **66**, 77-96.

Kelly, C.A., Rudd., J.W.M., Hesslein, R.H., Schindler, D.W., Dillon, P.J., Driscoll, C.T., Gherini, S.A. and Hecky, R.E. (1987) Prediction of biological acid neutralization in acid sensitive lakes. *Biogeochemistry* **3**, 129-140.

Kreiser, A.M., Patrick, S.T. and Battarbee, R.W. (1993) In M. Hornung and R.A. Skeffington (Eds.): *Critical Loads: Concept and Applications.* ITE Symposium No.28, HMSO, London, pp. 94-98.

Langan, S.J. and Wilson, M.J. (1994) Critical loads of acid deposition on Scottish soils. *Water, Air and Soil Pollution* **75**, 177-191.

Lein. L., Raddum, G.G. and Fjellheim, A. (1992) *Critical loads of acidity to freshwater - fish and invertebrates.* Fagrapport No. 23, NIVA, Oslo, Norway, 36pp.

Posch, M., Kämäri, J., Forsius, M., Henriksen, A. and Wilander, A. (1997) Exceedance of critical loads for lakes in Finland, Norway, and Sweden: reduction requirements for acidifying nitrogen and sulphur deposition. *Environmental Management* **21(2)**, 291-304.

Reynolds, B., Ormerod, S.J. and Gee, A.S. (1994) Spatial patterns in stream nitrate concentrations in upland Wales in relation to catchment forest cover and forest age. *Environmental Pollution* **84**, 27-33.

RGAR (1997) *Acid deposition in the United Kingdom 1992-1994.* Fourth Report of the Review Group on Acid Rain, June 1997. AEA Technology plc, Culham, UK, 176pp.

Seip, H.M. (1980) Acidification of freshwater - sources and mechanisms. In D. Drabløs and A. Tollan (Eds.) *Ecological impact of acid precipitation.* Proceedings of an international conference, Sandefjord, Norway, March 11-14, 1980. SNSF Project, Oslo, Norway, pp. 358-365.

Stoddard, J.L. (1994) Long-term changes in watershed retention of nitrogen: its causes and aquatic consequences. In L.A. Baker (Ed.), *Environmental Chemistry of Lakes and Reservoirs.* ACS Advances in Chemistry Series No. 237, American Chemical Society, Washington, D.C., pp.223-284.

Sverdrup, H., Warfvinge, P., and Nihlgård, B. (1994) Assessment of soil acidification effects on forest growth in Sweden. *Water, Air and Soil Pollution* **78**, 1-36.

UBA (1996) *Manual on methodologies and criteria for mapping critical levels/loads and geographical areas where they are exceeded.* Report for the UN ECE Convention on Long Range Transboundary Air Pollution. Texte 71/96, Federal Environment Agency (Umweltbundesamt), Berlin, Germany, 142 pp plus Appendices.

UNECE (1994) *Protocol to the 1979 Convention on Long Range Transboundary Air Pollution on Further Reduction of Sulphur Emissions.* Document ECE/EB.AIR/40. UNECE, New York and Geneva, 106 pp.